Fischer-Type Carbene Complexes of Tris(1,4-phenylene)amines and Tri(2-furyl)phosphine

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ABSTRACT: Novel chromium and tungsten mono- and multi-ethoxycarbene complexes were synthesized from tris(4-bromophenyl)amine and tri(2-furyl)phosphine substrates. A comparative study between the amine and phosphine multicarbene complexes revealed small differences between the respective compounds. In solution, an equilibrium situation was observed between the mono- and bis-carbene complexes of tri(2-furyl)phosphine. The monocarbene amine ligand differs from the analogous phosphine ligand in the way the heteroatom lone pair electrons are able to interact with the carbene functionality. Unlike for the phosphine, the greater electron delocalization of the amine affected the coordination ability of the ligand when reacted with [Pt(COD)Cl₂]. These properties of the monocarbene-carrying ligands were confirmed and supported by solid state structural studies, spectroscopic data, and density functional theory (DFT) calculations.

INTRODUCTION

It is already 50 years since the discovery of the first transition metal alkoxycarbene complex by Fischer and Maasbui̇l which kick-started research in areas associated with the metal–carbon double bond in particular and organometallic chemistry in general. Applications until now have been mostly devoted to organic transformations and template reactions of mononuclear Fischer carbene complexes.2–8 In recent years, research in organometallic chemistry has shifted toward the synthesis and properties of macromolecules and applications of metal–organic frameworks, dendrimers, nanoparticles, polymers, etc.9–12 Lately, Fischer carbene functionalities in small multicarboene—metal and multimetal—carbene complexes have come to the forefront and have been reported for biscarbene rods,13–16 small clusters, or structured carbene macro molecules.17–22 However, they lack the potential to impact in the above areas of material research because of challenging aspects associated with the synthesis of Fischer multicarbene complexes.23 As a result, the incorporation of a large number of Fischer carbene functionalities into transition metal macromolecular frameworks remains largely unexplored.

In this study, our approach was first to synthesize Fischer carbene complexes as substituents of common ligands such as amines or phosphines to investigate the effect multiple Fischer carbene complexes will have on each other and on the electron lone pair on the amine-N and phosphine-P. Second, we wished to transport the Fischer carbene functionality into the vicinity of the coordination sphere of other metals via the ligand heteroatom, in effect exploring electronic and steric features of amine-N and phosphine-P ligands in alkoxycarbene complexes that play a role when Fischer carbene complexes are “piggybacked” into larger macromolecules. Two ligands were chosen which contain aromatic substituents known to stabilize electrophilic Fischer carbene carbons via π-electron delocalization,24 namely, tris(4-bromophenyl)amine (N(C₆H₄Br)₃) and tri(2-furyl)phosphine (PFur₃). The triarylamidine backbone has been known for being used as dyes in photoreceptors and electroactive materials when attached to appropriate substituents25–27 and displays charge transfer and reversible redox properties with metal-containing substituents.28 Tris(4-bromophenyl)amine has three halogenated sites where site-specific carbene synthesis can be executed.29 The particular phosphine that was chosen contains furyl groups which are known to be able to readily form Fischer carbene complexes at the acid sites of the ring (position 2 and 5).30 Even though a furyl group is known to be an electron-withdrawing group due to the influence of the oxygen atom in the ring, it is also an electron rich system due the presence of 6 π-electrons in a 5-membered ring.31 The tri(2-furyl)phosphine ligand itself plays an important role as an ancillary ligand in coordination chemistry and in catalysts that facilitate metal–organic synthesis.32 Thus, making use of the acidic properties of the protons at the 5-positions of the furyl rings, PFur₃ is ideal for Fischer carbene synthesis.

The carbene carbon atom is linked to the nitrogen or phosphorus atom via a π-conjugated phenylene or furylene linker and can affect the bonding properties of the nitrogen or phosphorus atoms in two possible ways (Figure 1). First, the strong electron-withdrawing properties of the pentacarbonyl-
Figure 1. Illustration of movement of electron density between the heteroatom and the carbene carbon affording extreme resonance structures I and II.

metal–carbene moiety can drain electron density away from the heteroatom via the π-conjugated spacer unit (I). This decrease in the availability of the LP electrons on the heteroatom will weaken the potential bonding properties of the ligand's donor-atom. Thus, the movement of electron density toward the carbene carbon can decrease the electron deficiency at the carbene carbon atom, which will have a stabilizing effect on the carbene carbon and lessen its reactivity. Alternatively, coordination by the heteroatom to a second transition metal can move electron density away from the carbene carbon enhancing the carbene’s electrophilicity and reactivity.

RESULTS AND DISCUSSION

Amine Ligands. The lithium–halogen exchange reactions of triarylamines are readily achievable at low temperatures with nBuLi. Lithiation of N(C₆H₄Br)₃ and subsequent addition of group 6 metal carbonyls (Cr/W) gave the corresponding metal acylates which, after treatment with the alkylation agent Et₃OBF₄, yielded the neutral carbene complexes (Scheme 1). The reaction afforded all three carbene complexes in addition to small amounts of the butylcarbene complex. The products were separated and isolated with a silica gel column in the sequence 1, 2, and 3.

To maximize the yields for the synthesis of the multicarbene complexes, it was found that a stepwise addition of the second and third equivalents of nBuLi followed by metal carbonyl addition is required. Addition of three equivalents of the alkylation agent afforded the neutral mono-, bis-, and tris-carbene complexes with the triphenyleneamine core, 1, 2, and 3, respectively (Scheme 1).

The complexes that were isolated were bright orange with color intensity increasing with the number of M(CO)₅ units attached to the original amine by carbene complex formation. The differences in the optical properties of the three different compounds are small compared to the notable differences in moving from the known monocarbene complex, [M(C(OEt)Fur)₃(CO)₅], to the corresponding biscarbene complex, [((CO)₅M(C(OEt))₃Fur)] (Fur = furylene), which changes from red to purple In several instances, one or two bromine atoms were replaced by a hydrogen atom, which complicated the ¹H NMR spectra of 1. For instance, 1a (the complex is analogous to 1a with bromine atoms replaced by hydrogen atoms in 30% yield) was isolated and found to form on the addition of excess amounts of Et₃OBF₄ during the alkylation step of the synthesis. The isolated carbene complexes were characterized by spectroscopic methods and the molecular structures confirmed by single X-ray crystallography for 1a, 1b, and 2b (see below).

NMR analysis of complexes 1–3 focuses on changes in the chemical shifts of the protons and carbons with an increase of carbene substituents. The chemical shift values in the ¹H NMR spectra of the α-protons is indicative of the deshielding and electron-withdrawing properties of the carbene substituent. These chemical shifts are found furthest downfield and become more shielded on moving from 1 (a, 7.66; b, 7.75 ppm) to 2 (a, 7.47; b, 7.63 ppm) to 3 (a, 7.38; b, 7.57 ppm) in the ¹H NMR spectra. The downfield shifts of the aromatic protons of the rings with the carbene complex substituents in 1(a,b)–3(a,b) are in general smaller (6.57–7.75 ppm) than that found in phenylethenamine ester compounds (7.21–8.03 ppm) and even more so for that recorded for a nitro substituent in the 4-position of phenylethenamines (6.95–9.10 ppm). The ¹³C NMR spectra of the compounds reveal that the carbene carbon signals move downfield as the number of carbene substituents on the molecule increase: 1 (a, 332.6; b, 308.6 ppm), 2 (a, 337.9; b, 311.1 ppm), 3 (a, 337.9; b, 312.6 ppm). In the ¹³C NMR spectra, metal–carbonyl resonances are metal-sensitive but are insensitive to the number of carbene substituents and

Scheme 1. Synthesis of Triphenyleneamine Mono(1), Bis(2), and Triscarbene(3) Complexes

![Scheme 1](image-url)
give similar \( \delta \)-values for 1, 2, and 3. The same is true for the vibrational frequencies in the IR spectra of 1, 2, and 3.

A comparative study of the bond distances in the solid state structures of 1a', 1b, and 2b indicate extended conjugated systems that stretch from the amine nitrogen to the carbene carbon atom (Figure 2). Compound 1a' reveal angles involving the central nitrogen atom that deviate only slightly from 120°, which indicates that the nitrogen lies in a flat plane with the phenylene carbons and the carbene carbon atom in the 4-position (Figure 3). The bond angles around the nitrogen atom closely resemble an sp\(^2\)-hybridized atom with the lone pair in a p-orbital. The latter is favorably oriented perpendicular to the plane of the ring to participate in the \( \pi \)-interaction with the bridging 1,4-phenylene \( \pi \)-cloud and the empty p\(_{\pi}\)-orbital of the carbene carbon atom.

The torsion angles of C9—C10—N13—C14 and Cr1—C6—C7—C8 are small with values of \(-4.4(2)° \) and \(0.9(2)°\), respectively. By contrast, Mills and Redhouse found that for \([(\text{CO})_5\text{Cr}{\text{C(OMe)Ph}}]\) the phenyl plane was roughly perpendicular to the p\(_{\pi}\)-orbital of the carbene carbon (101.1°). This implies that the \( \pi \)-electron system of the carbene and ring in A(a) did not interact. Another difference between compound 1a' and A(a) is the angle around the carbene carbon atom with angle values for Cr-Carbene-O of 126.9(1)° (A(a): 134(2)°), for the C\(_{\text{Ph}}\)-Carbene-O of 105.9(1)° (A(a): 104(2)°), and for C\(_{\text{Ph}}\)-Carbene-Cr of 127.2(1)° (A(a): 122(1)°). Selected bond and torsion angles of 1a' are listed in Table 1.

The delocalization of the nitrogen lone pair via the bridging phenylene is manifested in alternating longer and shorter bond distances in the benzene ring, while this is not the case for C—C bond distances of the two unsubstituted phenyl rings which are all the same. The bond between the nitrogen and the phenyl ring, C10—N13 (1.378(3) Å), is significantly shorter compared to that of the other nitrogen—carbon(phenyl) bonds, C14—N13 (1.446(2) Å), and C20—N13 (1.434(3) Å).

We have further compared complexes 1a’ and A(a) with the help of density functional theory (DFT) calculations. The most relevant bond distances and corresponding Wiberg bond indices (WBI’s) are shown in Figure 4. In good agreement with the structural analysis commented above, our calculations reveal that the presence of the nitrogen atom in 1a’ provokes a clear shortening of the C-Carbene—Caryl bond (the corresponding

![Figure 2. Selected bond lengths of 1a' showing alternating longer—shorter bond distances in the phenylene linker between the amine-N and carbene-C atoms.](image)

![Figure 3. Solid-state structure of 1a'. Ellipsoids were set at 50% probability; hydrogen atoms were omitted for clarity. (See Figure 2 for important bond lengths.)](image)

Table 1. Selected Bond Angles (deg) and Torsion Angles (deg) for 1a’

<table>
<thead>
<tr>
<th>bond angles (deg)</th>
<th>atoms</th>
<th>torsion angles (deg)</th>
<th>atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>126.9(1)</td>
<td>Cr1—C6—O6</td>
<td>0.9(2)</td>
<td>Cr1—C6—C7—C8</td>
</tr>
<tr>
<td>127.2(1)</td>
<td>Cr1—C6—C7</td>
<td>1.9(2)</td>
<td>O6—C6—C7—C12</td>
</tr>
<tr>
<td>105.9(1)</td>
<td>O6—C6—C7</td>
<td>0.8(3)</td>
<td>C7—C8—C9—C10</td>
</tr>
<tr>
<td>120.5(1)</td>
<td>C10—N13—C14</td>
<td>179.3(2)</td>
<td>C8—C9—C10—N13</td>
</tr>
<tr>
<td>122.6(1)</td>
<td>C10—N13—C20</td>
<td>4.4(2)</td>
<td>C9—C10—N3—C14</td>
</tr>
<tr>
<td>116.3(1)</td>
<td>C14—N13—C20</td>
<td>180.0(2)</td>
<td>C12—C11—C10—N13</td>
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</tbody>
</table>
WBI increases from 1.082 to 1.147 from A(a) to 1a′ with the concomitant lengthening of the Cr–C carbene bond (the corresponding WBI decreases from 0.905 to 0.862 from A(a) to 1a′). The same trend is found for complex 1a (see Figure 4). This is due to the delocalization of the nitrogen atom LP into the system, which increases the contribution of the resonance structure depicted in Figure 2 in the description of the ground state of 1a′ (and 1a). Indeed, the second order perturbation theory (SOPT) of the natural bond orbital (NBO) method indicates a clear stabilizing delocalization of the LP of the nitrogen atom into the $\pi^*$ moiety of the adjacent aryl fragments. Interestingly, for 1a′ this delocalization is clearly stronger into the aryl fragment directly attached to the pentacarbonyl-carbene moiety (associated SOPT energy, $\Delta E^{(2)}$, of $-30.2$ kcal/mol) than into the other phenyl substituents ($\Delta E^{(2)} = -14.1$ and $-13.6$ kcal/mol, respectively). This is a direct consequence of the well-known strong electron-withdrawing ability of the (CO)$_5$M=C group, which behaves in a manner similar to that of a Lewis acid complexed carbonyl function.$^{33-35,42}$ Similar SOPT energies have been computed for the analogous complex 1a ($\Delta E^{(2)} = -31.2$ kcal/mol vs $-14.8$ and $-15.1$ kcal/mol).

In Figure 5, the solid state structures of 1b and 2b are shown and in general correspond with the structural features of 1a′.
The bond distances and angles around the nitrogen and carbene carbon atoms in 1b and 2b correspond well with those found for 1a, taking into account the difference in size of the W and Cr atoms. These data support previous conclusions about the delocalization of the nitrogen lone pair over the phenylene rings toward the carbene carbon atoms and the bond angles around the nitrogen and carbene carbon atoms. When comparing 1b and 2b, the above effects are observed for two carbene–phenylene–nitrogen fragments rather than one. Further, the torsion angle, \(W-C_{carbene}-C_{phenyl}-C_{14}\) in 1b has a value of 11.2(4)°, while the corresponding bonds have torsion angles of 33.3(4)° and 29.8(4)° in 2b, indicating the loss of planarity of 1b and 2b between the phenyl ring and carbene carbon atom, which we ascribed to less \(\pi\)-interaction. A general trend of the same nature was observed in the solid state structures of 1b and 2b (Figure 5). Particularly, they exhibit similar \(C_{carbene}-C_{aryl}\) bond lengths (ranging from 1.480 to 1.486 Å) thus confirming the partial double-bond character of this bond as a consequence of the delocalization of the LP of the nitrogen atom. The most significant difference between these structures and 1a, excluding the presence of the bromine substituents at the 4-positions of the rings, are the \(N-C_{phenyl}\) with carbene substituent bond lengths. In 1a, the bond length is 1.387(3) Å, while the value for the same bond in 1b is 1.398(4) Å and respective values of 1.410(3) and 1.416(3) Å in 2b. This can be ascribed to the lower electron-withdrawing ability of the \((CO)\_W\_carbene\) fragment as a consequence of 1.398(4) Å and respective values of 1.410(3) and 1.416(3) Å in 1b and 2b, respectively, according to previous studies on related carbene carbon atoms in transfer (MLCT) absorption, a spin-allowed ligand-moiety induces a strong bathochromic shift in the MLCT band of 1b and 2b, indicating less \(\pi\)-interaction. The bond distances and angles around the nitrogen and carbene carbon atoms. When comparing 1b and 2b, the above effects are observed for two carbene–phenylene–nitrogen fragments rather than one. Further, the torsion angle, \(W-C_{phenyl}-C_{carbene}-O\) in 1b has a value of 11.2(4)°, while the same bonds have torsion angles of 33.3(4)° and 29.8(4)° in 2b, indicating less \(\pi\)-interaction between phenyl ring and the carbene complex and loss of planarity of 1b and 2b between the phenyl ring and carbene carbon.

A "push–pull" feature between the \(\pi\)-donor nitrogen lone pair and the \(\pi\)-acceptor carbene carbon of complexes 1–3 should display different electronic properties when compared to those of the parent \([(CO)\_2\_Cr\_((OMe)\_Ph)]\) (A(a)). The UV–vis spectra of compounds 1–3 and A(a) (see Figure 6 and Table 2) exhibit three distinct low-lying bands centered at 456–476 nm, 370–382 nm, and 240 nm, which can be tentatively assigned to a spin-forbidden metal-ligand charge-transfer (MLCT) absorption, a spin-allowed ligand-field (LF-1) absorption, and one additional ligand-field (LF-2) transition, respectively, according to previous studies on related alkoxy carbene complexes.\(^{43–46}\) While the intense LF band remains practically unaltered in complex A(a) (\(\lambda_{\text{max}} = 252\) nm), the corresponding MLCT band appears at a much shorter wavelength (\(\lambda_{\text{max}} = 403\) nm). This indicates that the delocalization of the LP of the nitrogen atom into the carbene moiety induces a strong bathochromic shift in the MLCT band.

\[(\Delta\lambda_{\text{max}} = 50–75\text{ nm}), \text{ as found in related push–pull Fischer carbene complexes.}^{42,47}\]

Time-dependent density functional theory (TD-DFT) calculations were effected on complexes A(a) and 1a to gain insight into the nature of the MLCT absorption. The computed vertical excitation energies concur reasonably well with the experimental data (see Table 2). These calculations ascribe the MLCT absorption in A(a) to the promotion of one electron from the HOMO–1 (a doubly occupied chromium-d atomic orbital) to the LUMO, which is mainly located at the \(p_z\) atomic orbital of the carbene carbon atom (see Figure 7). Similarly, the MLCT band in 1a is ascribed by the TD-DFT calculations to the HOMO–1 \(\rightarrow\) LUMO vertical transition; however, in this case this transition overlaps with the intense (according to the corresponding computed oscillator strength) HOMO \(\rightarrow\) LUMO absorption. As shown in Figure 7, whereas the HOMO–1 of 1a is also located at the transition metal and the LUMO at the carbene carbon atom, the HOMO can be considered as the LP of the nitrogen atom. Therefore, the broad absorption observed in the range of 456–476 nm for complexes 1–3 is the result of a combination of a MLCT transition (resulting from the HOMO–1 \(\rightarrow\) LUMO vertical transition) and a LF transition (resulting from the HOMO \(\rightarrow\) LUMO vertical transition).

**Phosphine Ligands.** The deprotonation reaction of tri(2-furyl)phosphine by nBuLi was accomplished by the same methodology as that for the multicarbene synthesis with N(4-\(C\_6\_H\_4\_Br\))\(_3\). The acidity of the proton at the 5-position of the ring is sufficient for deprotonation followed by metal acylate formation after the addition of chromium or tungsten hexacarbonyl to give the carbene precursors. Alkylation with Et\_2OBF\(_4\) in the last step afforded 4–6 in reasonable to good yields (Scheme 2). A stepwise procedure was again employed to optimize the yields of 5 and 6. Complex 5 was the least stable and afforded in solution 4 and PFur\(_4\).

In addition to the major products 4, 5, and 6, three other carbene complexes, 7, B, and C were unexpectedly formed during the reaction and could be isolated and characterized from the reaction mixture (Scheme 3). The formation of 7, 2-monocarbene \([	ext{M(C(OEt)}\_2\_Fur}\_\{\text{CO}\}_\_3]\) complex (B), and 2,5-bis carbene complex \([\{\text{M(C(OEt)}\_2\_Fur}\}_\_3]\) (C) can be explained by the presence of excess nBuLi in the reaction mixture. A plausible interpretation involves a furyl metal acylate intermediate (I) being subjected to a nucleophilic displacement reaction by the butyl group of nBuLi. It was assumed that in I
the P-furyl bonds are weakened allowing for their cleaving during nBuLi addition. The resulting intermediates are the butyl-phosphine metal acylate (II), which is the precursor of 7, and a lithiated furyl compound (III), which after subsequent alkylation gives the red furylcarbene complex, B. Deprotonation by a second equivalent nBuLi of III gives IV while I gives V, which are the precursors of the purple furylène biscarbene complex C.

Assignments of the furyl ring proton signals in the $^1$H NMR spectra were based on the chemical shifts, their patterns and the magnitude of $^{31}$P-coupling constants displayed by a particular ring proton in the $^1$H and $^{13}$C NMR spectra. The protons furthest downfield in the $^1$H NMR spectra were assigned to the proton in the 5-position of the unsubstituted furan rings. Small downfield shifts were observed in the $^1$H NMR spectra of the furyl rings for the protons in going from PFur$_3$ to 4. The $^1$H

Table 2. Comparison of the UV/Vis Excitation Energies (in nm) of Compounds 1−3$^a$

<table>
<thead>
<tr>
<th></th>
<th>LF-2</th>
<th>LF-1</th>
<th>MLCT</th>
</tr>
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<tbody>
<tr>
<td>A(a)</td>
<td>232</td>
<td>403</td>
<td>403 (377, 0.214, HOMO−1→LUMO)$^b$</td>
</tr>
<tr>
<td>1a</td>
<td>245</td>
<td>372</td>
<td>456 (468, 0.067, HOMO−1→LUMO)$^b$ (440, 0.695, HOMO→LUMO)$^b$</td>
</tr>
<tr>
<td>2a</td>
<td>245</td>
<td>382</td>
<td>467</td>
</tr>
<tr>
<td>3a</td>
<td>243</td>
<td>388</td>
<td>467</td>
</tr>
<tr>
<td>1b</td>
<td>244</td>
<td>372</td>
<td>457</td>
</tr>
<tr>
<td>2b</td>
<td>239</td>
<td>378</td>
<td>476</td>
</tr>
<tr>
<td>3b</td>
<td>241</td>
<td>370</td>
<td>475</td>
</tr>
</tbody>
</table>

$^a$The first value corresponds to experimental data (recorded at room temperature in CH$_2$Cl$_2$ with a concentration of 0.00001 M). In parentheses, the first value corresponds to the computed PCM(CH$_2$Cl$_2$)-TD-B3LYP/def2-TZVP vertical excitation energy, and the second value is the corresponding oscillator strength. $^b$Time-dependent (TD)-DFT vertical transition assigned to the observed band.
NMR chemical shifts for the protons of the furyl rings with or without carbene substituents and the ethoxycarbene substituents generally remained approximately the same in spite of the number of carbene substituents increasing from one (4) to two (5) to three (6). This was supported by similar values found for the resonances in the $^1$H and $^{13}$C NMR spectra for the WC(OEt)Fur-unit and the complexes $4b$−$6b$. The carbene carbon chemical shifts in the $^{13}$C NMR spectra are insensitive on increasing the number of carbene substituents and remain the same. The $^{31}$P NMR resonances move slightly downfield as the number of carbene substituents increase in the complexes from one to two to three; however, there is a negligible difference between the chromium and tungsten resonances of the respective compounds (4, Cr −72.8, W −72.7 ppm; 5, Cr −69.6, W −69.4 ppm; 6, Cr −63.5, W −63.2 ppm). From this data, it is clear that the carbene moiety as a substituent does not significantly affect the bonding properties of the phosphorus atom of the phosphine.

Furthermore, measurement of the NMR spectra of both 4a and 4b in CDCl$_3$ over time revealed the presence of three other compounds (Scheme 3).

Figure 8. $^{31}$P NMR spectrum of 4b in CDCl$_3$ solution.
product 4b (−72.8 ppm), small amounts of 5b (−69.5 ppm) and PFur3 at −77.8 ppm (upfield from the reported value of −76.8 ppm) as well as a downfield peak at −11.7 ppm (vide supra 8b) are observed. The formation of the minor product, 5, is interesting and can be explained by a reaction of 4 to form 5 and PFur3, which are always present in any solution of 4 (Scheme 4). The equilibrium between 4 and 5 in solution lies far to the left (Scheme 4), based on 31P NMR peak intensities. The 1H NMR spectrum of 4b displays two sets of signals of different intensities (4b:8b, 19:1) and at distinctly different chemical shift values for all the signals. Since the chemical shifts of PFur3, 4b, and 5b are very similar, the dramatic downfield shift of the final signal in the 31P NMR is indicative of a phosphine phosphorus atom coordinated to a second transition metal (8b, Figure 9). A duplication of the M(CO)5-pattern of bands for the carbonyl vibrational frequencies was observed in the IR spectrum and clearly indicates the different bonding properties of carbene (4b) and phosphine ligands (8b). The observation that phosphines can displace carbonyl ligands in situ to afford coordination compounds is not new, and examples involving a Fischer carbene complex are known.17,48−50

The solid state structure of 4b shows a trigonal pyramidal arrangement of substituents around the phosphorus atom, while the electron lone pair takes up the fourth position (Figure 10). The metal−carbene bond is slightly out of the plane of the furyl ring with the W1−C6−C9−O7 torsion angle at 8.4(2)°. A comparative study among the solid state structures of 4b, PFur3, and B(b) (Table 3) provides an indication of the overall effect that the Fischer carbene substituent has on the properties of the phosphine. The most significant differences are found in the bond distances of the furyl ring attached to the carbene substituent compared to the distances of the other furyl rings, which are the same as those for PFur3. These differences become greater as one approaches the carbene carbon and are indicative of a localized stabilization of the carbene carbon by this furyl ring. There are three striking differences between the solid state structures of B(b) and 4b: first, the planar arrangement of substituents around the carbene carbon in B(b) (W−C6−C5−C4: 0.00(6)°) compared to a corresponding torsion angle of 8.4(2)° for 4b; second, a remarkable difference in the bond lengths of the Ccarbene−O(Et) bond and the Ccarbene−Cfuryl bond of 4b and B(b) reveals an alternate way of stabilization of the carbene carbon in the two compounds; and third, the presence of much longer C−O distances in the furyl ring of B(b) compared to those of 4b.

Again, we have further compared compounds 4b, B(b), and PFur3, with the help of DFT calculations. As shown in Figure 11, the W=Ccarbene and Ccarbene−Cfury distances remain practically unaltered when comparing compound 4b to the analogous [(CO)5W=C(OEt)Fur] complex, B(b). This confirms that the metal−carbene fragment is not affected by the presence of the phosphine fragment. Notably, the P−Cfury distance containing the carbene fragment is not affected by the presence of the phosphine fragment. Notably, the P−Cfury distance containing the carbene fragment is not affected by the presence of the phosphine fragment.

Figure 9. Coordination of 4b to form a bimetallic compound 8b.

Figure 10. Solid-state structure of 4b. Ellipsoids were set at 50% probability; hydrogen atoms were omitted for clarity.
further support for the lack of direct conjugation between the LP and the carbene moiety.

Interestingly, as a consequence of the π-conjugation between the furyl substituent and the electrophilic carbene carbon atom in 4b (which significantly alters the C–C and C–O distances of the furyl group attached to the carbene), the delocalization of the phosphorus LP into the adjacent σ*(C–O) molecular orbital observed in the free PFur3 is reduced in complex 4b (associated SOPT-energy, ΔE(2) = −9.7 kcal/mol in PFur3 vs ΔE(2) = −8.2 kcal/mol in 4b; Figure 12). This indicates that the phosphorus LP in complex 4b is even more available than in the free phosphine, thus increasing its electron-donating ability. On the basis of these findings, we anticipated that the otherwise reactive Fischer carbene moiety would more than likely remain intact during coordination of the phosphine-carrying carbene to other metals.

The wavelengths of the absorption maxima of the phosphine series are listed in Table 4. The values did not reveal any significant differences between the compounds, again illustrating the absent effect of the increasing number of carbenes on the molecular system of each compound. Not surprisingly, there is a clear difference between the wavelengths of the LF and MLCT transfers of the two different metals, with average values of 319 and 330 nm for the LF transition as well as 477 and 455 nm for the MLCT transition of the respective chromium and tungsten analogues.

TD-DFT calculations were effected on complex 4b to gain insight into the nature of the MLCT absorption. In this case, our calculations ascribe the MLCT absorption to the promotion of one electron from the HOMO−1 to the LUMO. As shown in Figure 13, the HOMO−1 is mainly centered at a d atomic orbital of tungsten, whereas the LUMO is centered at the pσ atomic orbital of the carbene carbon atom. Strikingly, no contribution of the LP of the phosphorus atom in

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Table 3. Comparison of Furan Ring Bond Distances** of PFur3, 4b, and B(b)**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond distances (Å)</th>
<th>Bond distances (Å)</th>
<th>Bond distances (Å)</th>
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<tbody>
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<td>P – C2</td>
<td>1.802(1)</td>
<td>1.801(3)</td>
<td>1.812(2)</td>
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<tr>
<td>O1 – C2</td>
<td>1.380(2)</td>
<td>1.378(4)</td>
<td>1.366(2)</td>
</tr>
<tr>
<td>C2 – C3</td>
<td>1.357(2)</td>
<td>1.358(4)</td>
<td>1.366(3)</td>
</tr>
<tr>
<td>C3 – C4</td>
<td>1.426(2)</td>
<td>1.422(4)</td>
<td>1.412(2)</td>
</tr>
<tr>
<td>C4 – C5</td>
<td>1.338(2)</td>
<td>1.333(4)</td>
<td>1.366(2)</td>
</tr>
<tr>
<td>C5 – O1</td>
<td>1.370(2)</td>
<td>1.372(4)</td>
<td>1.376(2)</td>
</tr>
<tr>
<td>C5 – C6</td>
<td>-</td>
<td>1.460(2)</td>
<td>1.353(11)</td>
</tr>
<tr>
<td>C6 – W</td>
<td>-</td>
<td>2.171(2)</td>
<td>2.199(3)</td>
</tr>
<tr>
<td>C6 – OEt</td>
<td>-</td>
<td>1.327(2)</td>
<td>1.406(1)</td>
</tr>
<tr>
<td>W–COon</td>
<td>-</td>
<td>2.049(4)</td>
<td>2.042(7)</td>
</tr>
<tr>
<td>W–COmes</td>
<td>-</td>
<td>2.031(2)</td>
<td>2.009(4)</td>
</tr>
</tbody>
</table>

**The average taken for similar rings in the same structure.

Figure 11. Optimized geometries of PFur3 and complexes 4b and B(b). Bond lengths are given in angstroms. Corresponding Wiberg bond indices are given in parentheses. All data were computed at the B3LYP/def2-TZVP level.

Figure 12. NBO-molecular orbitals responsible for the delocalization of the phosphorus lone-pair.
used as a node in organometallic frameworks.  

platinum fragment as acceptor was chosen because it is widely anticipated that the phosphine ligand structural data, features, and theoretical calculations, we center (without a 

into the vicinity of the coordination sphere of the second metal. The coordinative properties of the (4b) and phosphine-P

the parent phosphine PFur3.

Coordination Properties of 1b and 4b. To investigate the coordination ability of the amine-N (1b) and phosphine-P (4b) ligands, we proceeded to test their coordinative properties to another metal center. The coordinative properties of the ideal carbene-carrying ligand should be such that it would be capable of piggybacking a fragile Fischer carbene functionality into the vicinity of the coordination sphere of the second metal center (without affecting the identity of either the ligand or the accompanying carbene complex). On the basis of the above structural data, features, and theoretical calculations, we anticipated that the phosphine ligand 4b compared to the amine 1b should be the better host of a carbene substituent. A platinum fragment as acceptor was chosen because it is widely used as a node in organometallic frameworks.  

The COD ligand in [Pt(COD)Cl2] was displaced by two molecules of 4b to give 9b after stirring for 18 h in CH2Cl2 in high yields (Scheme 5). By contrast, the analogous reaction with 2 mol equiv of 1b did not give the corresponding platinum−bisamine−carbene complex. Spectroscopic measurements of the product mixture revealed the presence of carbene transfer and carbene−carbene coupling products. The formed products support the catalytic role of the platinum metal center. It is well-known that platinum and palladium complexes can participate in carbene transfer reactions and carbene−carbene coupling reactions.  

The coordination of 4b to Pt resulted in downfield shifts of the 31P NMR resonances to −35.3 ppm with a (195Pt{31P}) coupling of 1847 Hz for 9b. The 1H NMR resonances of the furyl rings, particularly the furyl group with the carbene substituent, did show a downfield shift with values of 7.11 (4b: 7.01) and 6.96 (4b: 6.65) ppm for the furylene linker, while significant shifts were also observed in the 13C NMR. Interestingly, the carbene carbon atom remains practically unaltered (δ = 284.0 ppm in 4b vs 286.4 in 9b). The above results indicate that the coordination of the phosphorus atom to the platinum center affects the properties of the phosphine ligand without modifying the electronic properties of the carbene moiety.

The molecular structure of 9b comprises two molecules of 4b coordinated, via the phosphorus atoms, in cis-positions of a square planar Pt complex, in spite of their bulkiness (Figure 14). The averaged C_Furyl−P−C_Furyl angle increases marginally in the order 101.3(1)° in 4b to 102.9(1)° in PFur3 and 104.4(2)° and 103.2(3)° in 9b, while the angles for P−Pt−P and Cl−Pt−Cl angles in 9b are 94.4(1)° and 87.7(1)°, respectively. The bond distances within the larger molecule show the same general trends as was observed for 4b. The two different ligands of 4b within the 9b are, however, not exactly the same. For example, the bond distances of the two C_furyl−C_carbene bonds have values of 1.468(8) and 1.449(8) Å and respective W−C_carbene bond distances of 2.160(5) and 2.183(6) Å. A reasonable explanation for the observation is the steric hindrance, which is illustrated in the solid state structure of 9b in Figure 14.

CONCLUSIONS

In conclusion, we have demonstrated that the multiple carbene moieties present in compounds 2, 3, 5, and 6 function independently of each other and are stable compounds. Further, we have shown how a common ligand such as a phosphine (PFur3) can be used to carry a reactive Fischer carbene moiety into the coordination sphere of a second transition metal (Pt). Through theoretical calculations we showed that in 4b, the phosphine’s coordinating abilities to other metals become stronger, while the carbene carbon atom’s bonding properties are hardly affected. The fact that in 4b, unlike for 1b, no inter- or intramolecular template reactions involving the carbene unit occurred in the presence of the platinum metal suggested that phosphines could successfully act as carbene-carrying agents. This was confirmed by the synthesis of 9b, which can be considered as the first step of a carbene-

Table 4. Comparison of the Main UV/Vis Excitation Energies of Compounds 4−6

<table>
<thead>
<tr>
<th></th>
<th>LF-2</th>
<th>LF-1</th>
<th>MLCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>483</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>313</td>
<td>475</td>
<td></td>
</tr>
<tr>
<td>6a</td>
<td>325</td>
<td>473</td>
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</tr>
<tr>
<td>4b</td>
<td>285</td>
<td>336</td>
<td>453</td>
</tr>
<tr>
<td>5b</td>
<td>286</td>
<td>326</td>
<td>457</td>
</tr>
<tr>
<td>6b</td>
<td>282</td>
<td>326</td>
<td>455</td>
</tr>
</tbody>
</table>

The first value corresponds to experimental data (recorded at room temperature in CH2Cl2 with a concentration of 0.00001 M). In parentheses, the first value corresponds to the computed PCM-(CH2Cl2)-TD-B3LYP/def2-TZVP vertical excitation energy, and the second value is the corresponding oscillator strength. *Time-dependent (TD)-DFT vertical transition assigned to the observed band.

This absorption was found, which sharply contrasts with the situation in amine-carrying complexes 1−3. Therefore, it can be safely concluded that whereas the LP of the nitrogen atom is not available for coordination in complexes 1−3, the scenario is completely different for the phosphine-carrying complexes 4−6, where the LP of phosphorus is even more available than in the parent phosphine PFur3.

![Computed molecular orbitals of complex 4b (isosurface value of 0.05 au).](image1)

Figure 13. Computed molecular orbitals of complex 4b (isosurface value of 0.05 au).
loading process preceding coordination studies on larger molecules or surfaces. Hence, conditions were met to use phosphine ligands as agents to piggyback Fischer carbene complexes into small macromolecules with potential application in metal organic frameworks and networks.

**EXPERIMENTAL SECTION**

**General.** Tris(4-bromophenyl)amine, tri(2-furyl)phosphine, Cr(CO)6, W(CO)6, and K2[PtCl4] were purchased from Sigma-Aldrich and Strem Chemicals and used as received. [Pt(COD)Cl2] was prepared from K2[PtCl4] by the procedure of Clark and Manzer,58 while Et3OBF4 was prepared according to the literature procedure by Meerwein.59 All operations were performed using standard Schlenk techniques under an atmosphere of nitrogen or argon. Silica gel 60 (particle size 0.0063−0.200 mm) was used as resin for all separations in column chromatography. Anhydrous THF and hexane were distilled over sodium metal and dichloromethane over CaH2. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on Bruker Ultrashield Plus 400 AVANCE 3 and Bruker Ultrashield 300 AVANCE 3 spectrometers using CDCl3 and C6D6 as solvents at 25°C. The NMR spectra were recorded for 1H at 400.13 and 300.13 MHz, 13C at 100.163 and 75.468 MHz, and 31P at 161.976 and 121.495 MHz. The chemical shifts were recorded in ppm, using deuterated solvent signals for internal references. For CDCl3 and C6D6, respectively, δH at 7.2400 and 7.1500 ppm, and δC at 77.000 and 128.000 ppm, and the 31P NMR spectra were referenced to the deuterated lock solvent which had been referenced to 85% H3PO4. Infrared spectroscopy was performed on a PerkinElmer Spectrum RXI FT-IR spectrophotometer with a NaCl cell, using hexane as solvent. X-ray crystallography was performed at 20 °C on a Siemens P4 diffractometer fitted with a Bruker 1 K CCD detector using graphite-monochromated, Mo−Kα radiation by means of a combination of phi and omega scans. UV/visible Spectroscopy was measured in a range of 200.0 to 1100 nm in a quartz cell with CH2Cl2 as reference and measured on a PerkinElmer Lambda 25 instrument with a Dell Optiplex 760 Intel Celeron CPU. Mass spectral analyses were performed on a Synapt G2 HDMS by direct infusion at 5 μL/min with positive electron spray as the ionization technique. The m/z values were measured in the range of 400−1500 with methanol as solvent.

**Synthesis of [M(CO)5C(OEt)C6H4]NPh2 (M = Cr 1a; W 1b), [M(CO)5C(OEt)C6H4]NPh (M = Cr 2a; W 2b), and [M(CO)5C(OEt)C6H4]N (M = Cr 3a; W 3b).** nBuLi (0.80 mL, 1.50 M, 1.20 mmol) was added to a cold solution (−78 °C) of tris(4-bromophenyl)amine (0.48 g, 1.00 mmol) dissolved in dry THF (30 mL). Upon lithiation, one equivalent M(CO)6 (Cr(CO)6: 1.00 mmol, 0.22 g) (W(CO)6: 1.00 mmol, 0.35 g) was immediately added and allowed to stir until all of the metal carbonyl was dissolved (45 min). The lithiation and reaction with M(CO)6 steps were repeated twice more. After the third lithiation and metal acylate formation, the solvent was removed in vacuo, and the residue dissolved in a minimum amount of CH2Cl2. Et3OBF4 (0.57 g, 3.0 mmol) dissolved in CH2Cl2 (30 mL) was added to the cold (−40 °C) reaction mixture. The resulting solution was filtered through silica gel, washed with CH2Cl2, and the solvent removed under vacuum. The fractions were isolated from a silica gel column using hexane and dichloromethane mixtures. The products were concentrated under reduced pressure, yielding three bright orange products. By changing the molar equivalents of nBuLi and M(CO)6 added, the yields of the major products can be controlled (Table 5). Compound 1a′ was isolated in a yield of 30% (0.37 g) when 1 equiv of nBuLi and M(CO)6 were added subsequently followed by 2 equivs of alkylation agent (all under the above specified reaction conditions).

**Table 5. Reaction Yields for n Subsequent Steps**

<table>
<thead>
<tr>
<th>n</th>
<th>Yield mass (%)</th>
<th>Yield mass (%)</th>
<th>Yield mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>0.21 g</td>
<td>32%</td>
<td>0.05 g</td>
</tr>
<tr>
<td>2a</td>
<td>0.16 g</td>
<td>20%</td>
<td>0.33 g</td>
</tr>
<tr>
<td>3a</td>
<td>0.16 g</td>
<td>16%</td>
<td>0.47 g</td>
</tr>
<tr>
<td>1b</td>
<td>0.32 g</td>
<td>41%</td>
<td>0.09 g</td>
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<tr>
<td>2b</td>
<td>0.26 g</td>
<td>24%</td>
<td>0.84 g</td>
</tr>
<tr>
<td>3b</td>
<td>0.30 g</td>
<td>22%</td>
<td>0.82 g</td>
</tr>
</tbody>
</table>

nBuLi and M(CO)6 were added to 1.00 mmol tris(4-bromophenyl)amine under specified reaction conditions (M = Cr(a), W(b)).
Crystals for 1a, 1b, and 2b were obtained from a CH₂Cl₂ solution layered with hexane after slow diffusion of hexane into the solution. Scheme 6 illustrates ¹H and ¹³C NMR numerical assignments of compounds 1–3.

Scheme 6. Numerical Proton and Carbon Assignments

1a: C₆H₂NO₂NCrBr₂. ¹H NMR (CDCl₃, 300 MHz) δ 7.66 (d, 9.0 Hz, 2H, H3), 6.98 (d, 7.2 Hz, 4H, H11), 6.93 (d, 7.1 Hz, 4H, H10), 6.78 (d, 9.0 Hz, 2H, H2), 4.71 (q, 7.1 Hz, 2H, H6), 1.04 (t, 7.0 Hz, 3H, H7). ¹³C NMR (CDCl₃, 75 MHz) δ 332.6 (C5), 233.8 (C8, trans), 217.2 (C8, cis), 152.1 (C4), 146.0 (C9), 144.5 (C1), 130.0 (C2), 129.7 (C11), 126.3 (C10), 125.1 (C12), 118.0 (C3), 76.5 (C6), 15.2 (C7). IR (cm⁻¹, hexane): 2064 (m), 1983 (w), 1950 (s). ESI-MS (15 V, positive mode): calcd for [M + H]⁺ 781.9010; found, 781.9045.

2a: C₆H₄O₂NCrBr₂. ¹H NMR (CDCl₃, 300 MHz) δ 7.66 (d, 9.0 Hz, 2H, H3), 6.44 (d, 8.9 Hz, 4H, H11), 6.93 (d, 6.6 Hz, 4H, H10), 6.87 (m, 2H, H12), 6.78 (d, 8.1 Hz, 2H, H2), 4.71 (q, 6.9 Hz, 2H, H6), 1.04 (t, 6.8 Hz, 3H, H7). ¹³C NMR (CDCl₃, 126 MHz) δ 332.3 (C5), 223.8 (C8), trans, 217.2 (C8, cis), 152.1 (C4), 146.0 (C9), 144.4 (C1), 130.1 (C2), 129.7 (C11), 126.3 (C10), 125.1 (C12), 117.9 (C3), 76.4 (C6), 15.2 (C7). IR (cm⁻¹, hexane): 2056 (m), 1984 (w), 1950 (s). ESI-MS (15 V, positive mode): calcd for [M + H]⁺ 857.8750; found, 857.8750.

3b: C₆H₂O₂WFu₂. ¹H NMR (CDCl₃, 300 MHz) δ 7.57 (d, 8.8 Hz, 6H, H3), 6.77 (d, 8.8 Hz, 6H, H2), 6.40 (q, 7.0 Hz, 6H, H6), 1.04 (t, 7.1 Hz, 6H, H7). ¹³C NMR (CDCl₃, 101 MHz) δ 312.6 (J_C,W = 52.1 Hz, C5), 203.2 (J_W,C = 57.6 Hz, C8, trans), 197.5 (J_W,C = 64.3 Hz, C8, cis), 150.2 (C4), 149.3 (C1), 130.1 (C3), 123.3 (C2) 79.8 (C6), 15.0 (C7). IR (cm⁻¹, hexane): 2058 (m), 1986 (w), 1952 (vs). ESI-MS (15 V, positive mode): calcd for [M + H]⁺ 1385.9738; found, 1385.9738.

Synthesis of [M(CO)₅(COEt)Fu]PFu₂ (M = Cr 4a; W 4b). [M(CO)₅(CO)₂Fu]PFu₂ (M = Cr 5a; W 5b), [M(CO)₅(CO)₂Fu]⁺ (M = Cr 6a; W 6b), [M(CO)₅(CO)₂Fu]PFu₂ (M = Cr 7a; W 7b) (Fu = C₆H₄O₂). nBuLi (1.25 mL, 1.60 M, 2.00 mmol) was added to a cold solution (−78 °C) of tri(2-furyl)phosphine (0.46 g, 2.00 mmol) dissolved in dry THF (40 mL) and allowed to stir for 10 min in a cold bath, after which the solution was allowed to stir at room temperature (50 min). Upon lithiation, the reaction mixture was cooled (−60 °C), and 1 equiv of M(CO)₅ ([Cr(CO)₅]: 2.00 mmol, 0.44 g) (W(CO)₅): 2.00 mmol, 0.70 g) was added. The mixture was removed from the cold bath and allowed to stir until all of the metal carbonyl was dissolved (45 min). The lithiation and reaction with M(CO)₅ steps were repeated. After the third lithiation and metal acylate formation, the solvent was removed in vacuo and the residue dissolved in a minimum amount of CH₂Cl₂, Et₂OBF₂ (0.48 g, 6.00 mmol) dissolved in CH₂Cl₂ (30 mL) was added to the cold (−40 °C) reaction mixture. The resulting solution was filtered through silica gel, washed with CH₂Cl₂, and the solvent removed under reduced pressure. The fractions were separated from a silica gel column using hexane and dichloromethane/methanol mixtures. The products were isolated and concentrated under reduced pressure, yielding six different products. By altering the molar equivalents of lithiation and reaction with M(CO)₅, the composition of the major products can be controlled (Table 6). Crystals for 4b

Table 6. Reaction Yields for n Subsequent Steps*:

<table>
<thead>
<tr>
<th>n</th>
<th>mass yield</th>
<th>mass yield</th>
<th>mass yield</th>
</tr>
</thead>
<tbody>
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<td>n</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>4a</td>
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<td>0.25 g</td>
<td>0.15 g</td>
</tr>
<tr>
<td>5a</td>
<td>0.32 g</td>
<td>0.22 g</td>
<td>0.35 g</td>
</tr>
<tr>
<td>6a</td>
<td>0.14 g</td>
<td>0.7%</td>
<td>0.23 g</td>
</tr>
<tr>
<td>7a</td>
<td>0.08 g</td>
<td>0.9%</td>
<td>0.16 g</td>
</tr>
<tr>
<td>8b</td>
<td>0.05 g</td>
<td>0.8%</td>
<td>0.13 g</td>
</tr>
<tr>
<td>9b</td>
<td>0.04 g</td>
<td>0.7%</td>
<td>0.09 g</td>
</tr>
<tr>
<td>4b</td>
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<td>0.74 g</td>
<td>0.30 g</td>
</tr>
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<td>0.17 g</td>
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<td>8b</td>
<td>0.11 g</td>
<td>0.12 g</td>
<td>0.10 g</td>
</tr>
<tr>
<td>9a</td>
<td>0.10 g</td>
<td>0.12 g</td>
<td>0.06 g</td>
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</table>

*nBuLi and M(CO)₅ were added to 2.00 mmol tri(2-furyl)phosphine (0.46 g, 2.00 mmol) dissolved in dry THF (40 mL) and allowed to stir for 10 min in a cold bath, after which the solution was allowed to stir at room temperature (50 min). Upon lithiation, the reaction mixture was cooled (−60 °C), and 1 equiv of M(CO)₅ ([Cr(CO)₅]: 2.00 mmol, 0.44 g) (W(CO)₅): 2.00 mmol, 0.70 g) was added. The mixture was removed from the cold bath and allowed to stir until all of the metal carbonyl was dissolved (45 min). The lithiation and reaction with M(CO)₅ steps were repeated. After the third lithiation and metal acylate formation, the solvent was removed in vacuo and the residue dissolved in a minimum amount of CH₂Cl₂, Et₂OBF₂ (0.48 g, 6.00 mmol) dissolved in CH₂Cl₂ (30 mL) was added to the cold (−40 °C) reaction mixture. The resulting solution was filtered through silica gel, washed with CH₂Cl₂, and the solvent removed under reduced pressure. The fractions were separated from a silica gel column using hexane and dichloromethane/methanol mixtures. The products were isolated and concentrated under reduced pressure, yielding six different products. By altering the molar equivalents of lithiation and reaction with M(CO)₅, the composition of the major products can be controlled (Table 6). Crystals for 4b

Scheme 7. Numerical Proton and Carbon Assignments

were isolated from a CH₂Cl₂ solution layered with hexane after slow diffusion of hexane into the solution. Scheme 7 illustrates ¹H and ¹³C NMR numerical assignments of compounds 4–7.
4a: C₆H₅O₂PcR. ¹H NMR (CDCl₃, 300 MHz) δ 7.67 (dd, J = 1.9, 0.7 Hz, 2H, H14), 6.85 (dd, J = 1.6, 0.3 Hz, 2H, H12), 6.51 (dd, J = 1.2, 1.8 Hz, 2H, H13), 1.51 (q, J = 7.1 Hz, 2H, H7), 1.60 (t, J = 7.1 Hz, 3H, H8), 1.31 (d, J = 1.8 Hz, C4), 111.0 (d, J = 1.3 Hz, C13), 111.1 (d, J = 1.8 Hz, C4), 111.0 (d, J = 7.1 Hz, C13), 75.6 (C7), 153.3 (C8). ¹³C NMR (CDCl₃, 75 MHz) δ 310.6 (C6), 224.9 (C9, trans), 216.9 (C9, cis), 167.1 (d, J = 5.0 Hz, C5), 160.4 (d, J = 3.3 Hz, C2), 146.5 (d, J = 3.5 Hz, C11), 123.1 (d, J = 3.0 Hz, C2), 120.8 (d, J = 3.3 Hz, C13), 111.1 (d, J = 1.8 Hz, C4), 111.0 (d, J = 7.1 Hz, C13), 75.6 (C7), 153.3 (C8). ¹⁵P NMR (121 MHz, CDCl₃), δ = −72.8. IR (cm⁻¹, hexane): 2060(m), 1990(w), 1944(vs). ESI-MS (15 V, positive mode, m/z): calculated for [M + H]+ 480.9781; found, 480.9801.

4b: C₂H₅O₂PcP. Mp: 48 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.67 (dd, J = 1.8, 0.9, 0.7 Hz, 2H, H14), 7.01 (dd, J = 3.7, 1.2 Hz, 1H, H8), 6.44 (dd, J = 3.4, 2.6, 0.8 Hz, 2H, H12), 6.65 (dd, J = 3.6, 0.2 Hz, 1H, H3), 6.44 (dd, J = 3.4, 2.6, 1.8 Hz, 2H, H12), 4.90 (q, J = 7.1 Hz, 2H, H7), 1.58 (t, J = 7.1 Hz, 3H, H8). ¹³C NMR (101 MHz, CDCl₃), δ = 128.4 (J = 5.0 Hz, C5), 128.4 (J = 7.0 Hz, C11), 121.1 (d, J = 2.1 Hz, C2), 120.4 (d, J = 1.9 Hz, C13), 110.0 (d, J = 1.3 Hz, C13), 75.6 (C7), 153.3 (C8). ¹⁵P NMR (121 MHz, CDCl₃), δ = −55.3. IR (cm⁻¹, hexane): 2069(m), 2000(w), 1958(m), 1952(vs). ESI-MS (15 V, positive mode, m/z): calculated for [M + H]+ 471.0301; found, 471.0308.

5b: C₂H₅O₂PcP. IR (cm⁻¹, hexane): 2070(m), 1982(w), 1957(s), 1948(vs). ESI-MS (20 V, positive mode, m/z): calculated for C₂H₅O₂PcP [M]⁺ 611.9806; found, 611.9896.

5a: C₆H₅O₂PcPCr. ¹H NMR (CDCl₃, 400 MHz) δ 7.73–7.75 (m, 1H, H14), 7.10–7.09 (m, 1H, H12), 6.96–6.99 (m, 2H, H4), 6.36 (dd, J = 3.6, 1.1 Hz, 2H, H3), 6.49 (dd, J = 3.2, 2.1 Hz, 1H, H13), 5.11 (q, J = 7.0 Hz, 4H, H7), 1.61 (t, J = 7.0 Hz, 3H, H8). ¹³C NMR (CDCl₃, 101 MHz) δ 313.6 (C6), 224.4 (C9, trans), 216.5 (C9, cis), 167.1 (d, J = 3.7 Hz, C5), 157.4 (d, J = 5.0 Hz, C11), 123.2 (d, J = 2.5 Hz, C2), 121.1 (d, J = 3.8 Hz, C13), 113.4 (c), 111.0 (d, J = 7.7 Hz, C13), 78.1 (C7), 153.8 (C8). ¹⁵P NMR (162 MHz, CDCl₃), δ = −72.7. IR (cm⁻¹, hexane): 2070(m), 1982(w), 1954(vs), 1947(vs). ESI-MS (20 V, positive mode, m/z) calculated for C₆H₅O₂PcPCr [M]⁺ 619.0301; found, 619.0301.
optimized at the DFT level using the B3LYP$^{61,62}$ functional with the triple-$ξ$ valence plus polarization basis set def2-TZVP$^{63}$ for all atoms. This protocol is denoted B3LYP/def2-TZVP. All compounds were characterized by frequency calculations$^{64}$ and have a positive defined Hessian matrix indicating that they are minima on the potential energy surface. Calculations of absorption spectra were accomplished by using the TD-DFT$^{65,66}$ method at the same level. TD-DFT calculations were performed in dichloromethane as solvent using the polarizable continuum model (PCM) method.$^{67}$ This protocol is denoted PCM(CH$_2$Cl$_2$)-TD-B3LYP/def2-TZVP. The assignment of the excitation energies to the experimental bands was performed on the basis of the energy values and oscillator strengths. The B3LYP Hamiltonian was chosen because it was proven to provide reasonable UV/vis spectra for a variety of chromophores$^{70}$ including Fischer carbene complexes$^{44,47}$ and other organometallic species.$^{71-73}$

Donor–acceptor interactions and WBI have been computed using the NBO method.$^{74-77}$ The energies associated with these two-electron interactions have been computed according to the following equation:

$$\Delta E(2)_{\phi\phi} = -n_\phi \left( \phi^*|\hat{F}|\phi \right)^2 \epsilon_{\phi} - \epsilon_{\phi}^*$$

where $\hat{F}$ is the DFT equivalent of the Fock operator, and $\phi$ and $\phi^*$ are two filled and unfilled NBOs having $\epsilon_\phi \gamma \epsilon_{\phi}^*$ and energies, respectively; $n_\phi$ stands for the occupation number of the filled orbital.

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Notes

The authors declare no competing financial interest.

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DEDICATION

This work is dedicated to Professor Cedric Holzapfel on the occasion of his 80th birthday.

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(41) See computational details.
(49) Landman, M.; Pretorius, R.; Buitendach, B. E.; van Rooyen, P. H.; Conradie, J. Organometallics 2013, 32, 5491–5503.
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NMR Spectra
1a' $^1$H NMR spectrum

*Solvent contaminant
$^{13}$C NMR spectrum
As discussed in the text, spectra of 1 were complicated by Br/H exchange.

* Solvent contaminant
1a $^{13}$C NMR spectrum

\[
\text{Br} \quad \text{Br} \\
\text{Cr(CO)}_5 \quad \text{OEt}
\]
As discussed in the text, spectra of 1 were complicated by Br/H exchange.

*Solvent contaminant
1b $^{13}$C NMR spectrum
2a  $^1$H NMR spectrum

*Solvent contaminant
$^{13}$C NMR spectrum
*Solvent contaminant
$^{13}$C NMR spectrum

![NMR Spectrum Image]

- Chemical structure: 
  - Formula: (OC)$_3$W
  - Description: 
    - Br
    - C=O
    - CDCl$_3$
$^1$H NMR spectrum

*Solvent contaminant
3a $^{13}$C NMR spectrum
$^1$H NMR spectrum

* Solvent contaminant
$\text{S15}$

$3b$ $^{13}$C NMR spectrum

![C NMR spectrum image]
4a  $^1$H NMR spectrum

Mixture: major peaks (4)
Minor peaks (5 and PFur$_3$)
See text
$^{13}$C NMR spectrum

4a
$^{31}$P NMR spectrum
$^{1}$H NMR spectrum
4b \(^{13}\)C NMR spectrum
4b $^{31}$P NMR spectrum
$^1$H NMR spectrum

\[
\begin{align*}
&7.71 & 7.68 & 7.63 & 7.60 & 7.57 & 7.54 & 7.51 & 7.48 & 7.45 & 7.42 \\
&5.90 & 5.87 & 5.84 & 5.81 & 5.78 & 5.75 & 5.72 & 5.69 & 5.66 & 5.63 \\
&5.60 & 5.57 & 5.54 & 5.51 & 5.48 & 5.45 & 5.42 & 5.39 & 5.36 & 5.33 \\
&5.30 & 5.27 & 5.24 & 5.21 & 5.18 & 5.15 & 5.12 & 5.09 & 5.06 & 5.03 \\
&5.00 & 4.97 & 4.94 & 4.91 & 4.88 & 4.85 & 4.82 & 4.79 & 4.76 & 4.73 \\
&4.70 & 4.67 & 4.64 & 4.61 & 4.58 & 4.55 & 4.52 & 4.49 & 4.46 & 4.43 \\
&4.10 & 4.07 & 4.04 & 4.01 & 3.98 & 3.95 & 3.92 & 3.89 & 3.86 & 3.83 \\
&3.80 & 3.77 & 3.74 & 3.71 & 3.68 & 3.65 & 3.62 & 3.59 & 3.56 & 3.53 \\
&3.50 & 3.47 & 3.44 & 3.41 & 3.38 & 3.35 & 3.32 & 3.29 & 3.26 & 3.23 \\
&3.20 & 3.17 & 3.14 & 3.11 & 3.08 & 3.05 & 3.02 & 2.99 & 2.96 & 2.93 \\
&2.90 & 2.87 & 2.84 & 2.81 & 2.78 & 2.75 & 2.72 & 2.69 & 2.66 & 2.63 \\
&2.60 & 2.57 & 2.54 & 2.51 & 2.48 & 2.45 & 2.42 & 2.39 & 2.36 & 2.33 \\
&2.30 & 2.27 & 2.24 & 2.21 & 2.18 & 2.15 & 2.12 & 2.09 & 2.06 & 2.03 \\
&2.00 & 1.97 & 1.94 & 1.91 & 1.88 & 1.85 & 1.82 & 1.79 & 1.76 & 1.73 \\
&1.70 & 1.67 & 1.64 & 1.61 & 1.58 & 1.55 & 1.52 & 1.49 & 1.46 & 1.43 \\
&1.40 & 1.37 & 1.34 & 1.31 & 1.28 & 1.25 & 1.22 & 1.19 & 1.16 & 1.13 \\
&1.10 & 1.07 & 1.04 & 1.01 & 0.98 & 0.95 & 0.92 & 0.89 & 0.86 & 0.83 \\
&0.80 & 0.77 & 0.74 & 0.71 & 0.68 & 0.65 & 0.62 & 0.59 & 0.56 & 0.53 \\
&0.50 & 0.47 & 0.44 & 0.41 & 0.38 & 0.35 & 0.32 & 0.29 & 0.26 & 0.23 \\
&0.20 & 0.17 & 0.14 & 0.11 & 0.08 & 0.05 & 0.02 & 0.00 & 0.00 & 0.00 \\
\end{align*}
\]
5a $^{13}$C NMR spectrum
5a $^{31}\text{P}$ NMR spectrum
$^1$H NMR spectrum

S25
$5b$ 

$^{13}$C NMR spectrum

![Diagram of $^{13}$C NMR spectrum with chemical shifts and molecular structure]
6a $^1$H NMR spectrum
6a $^{13}$C NMR spectrum
Peak indicates coordination of 6a to [Cr]
$^1$H NMR spectrum
$^{13}$C NMR spectrum
$^{31}$P NMR spectrum
Compounds 7a and 7b are oils. Poor resolution of butyl peaks are caused by $^2J_{PH}$ coupling and the chirality of P when coordinated.

7a $^1$H NMR spectrum
$^{13}$C NMR spectrum
$^{31}$P NMR spectrum

7a

\[
\begin{array}{c}
\text{Phosphorus atom} \\
\text{Et group} \\
\text{Cr(CO)$_5$ group}
\end{array}
\]
7b $^1$H NMR spectrum
$^{13}$C NMR spectrum

- Peak at 195.8 ppm
- Peak at 78.52 ppm
- Peak at 76.88 ppm
- Other peaks at various ppm values
8b  $^1$H NMR spectrum
Mixture of 4b, 5b, PFur$_3$ and 8b: Please refer to text. Chemical shift values for 8b indicated.
$^1$H NMR spectrum
$^{13}$C NMR spectrum
$^{31}$P NMR spectrum
B(a)\(^1\) H NMR spectrum
B(a) \textsuperscript{1} $^{13}$C NMR spectrum

\[ \text{OEt} \quad \text{Cr(CO)}_5 \text{O} \]

\[ \text{CDC}l_3 \]
B(b)\textsuperscript{1}\textsuperscript{1} H NMR spectrum
B(b)\textsuperscript{1} $^{13}$C NMR spectrum
C(a) $^1$H NMR spectrum
# XRD Data and Parameters

## Table S1. Crystal data for complexes 1a’, 1b and 2b.

<table>
<thead>
<tr>
<th></th>
<th>1a’</th>
<th>1b</th>
<th>2b</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C_{26}H_{19}CrNO_{6}</td>
<td>C_{26}H_{17}Br_{2}NO_{6}W</td>
<td>C_{34}H_{22}BrNO_{12}W_{2}</td>
</tr>
<tr>
<td><strong>Formula weight (g/mol)</strong></td>
<td>493.42</td>
<td>783.07</td>
<td>1084.13</td>
</tr>
<tr>
<td><strong>Temperature (K)</strong></td>
<td>100(2)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td><strong>Colour</strong></td>
<td>Orange</td>
<td>Orange</td>
<td>Red-black</td>
</tr>
<tr>
<td><strong>Wavelength (Å)</strong></td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>triclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P -1</td>
<td>C 2/c</td>
<td>P 2/c</td>
</tr>
<tr>
<td><strong>Unit cell dimensions (Å, °)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>9.2423(6)</td>
<td>51.9931(16)</td>
<td>19.5309(13)</td>
</tr>
<tr>
<td>b</td>
<td>9.7790(7)</td>
<td>6.4100(2)</td>
<td>22.5776(15)</td>
</tr>
<tr>
<td>c</td>
<td>13.6276(9)</td>
<td>15.6570(5)</td>
<td>7.9946(5)</td>
</tr>
<tr>
<td>α</td>
<td>82.9800(10)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β</td>
<td>71.6530(10)</td>
<td>95.9360(12)</td>
<td>90.262(2)</td>
</tr>
<tr>
<td>γ</td>
<td>82.6000(10)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>Volume (Å³)</strong></td>
<td>1154.95(14)</td>
<td>5190.1(3)</td>
<td>3525.3(4)</td>
</tr>
<tr>
<td><strong>Density (calculated) (Mg/m³)</strong></td>
<td>1.419</td>
<td>2.004</td>
<td>2.043</td>
</tr>
<tr>
<td><strong>Absorption coefficient (mm⁻¹)</strong></td>
<td>0.538</td>
<td>7.572</td>
<td>7.717</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>508</td>
<td>2976</td>
<td>2048</td>
</tr>
<tr>
<td><strong>Crystal size (mm³)</strong></td>
<td>0.36 x 0.26 x 0.18</td>
<td>0.370 x 0.149 x 0.022</td>
<td>0.433 x 0.095 x 0.048</td>
</tr>
<tr>
<td><strong>θ range for data collection</strong></td>
<td>2.77 to 28.34</td>
<td>2.363 to 30.507</td>
<td>2.272 to 30.520</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>h</td>
<td>-12 – 12</td>
<td>-74 – 74</td>
</tr>
<tr>
<td>k</td>
<td>-12 – 12</td>
<td>-9 – 9</td>
<td>0 – 32</td>
</tr>
<tr>
<td>l</td>
<td>-18 – 17</td>
<td>-22 – 22</td>
<td>0 – 11</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>13933</td>
<td>7933</td>
<td>15782</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>5513 [R(int) = 0.0256]</td>
<td>7933 [R(int) = 0.0539]</td>
<td>13593 [R(int) = 0.0436]</td>
</tr>
<tr>
<td><strong>Completeness to θ = 25.242°</strong></td>
<td>99.80%</td>
<td>100.00%</td>
<td>99.90%</td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
<td>Full-matrix least squares on F²</td>
<td>Full-matrix least squares on F²</td>
<td>Full-matrix least squares on F²</td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>5513 / 0 / 308</td>
<td>7933 / 0 / 326</td>
<td>15782 / 0 / 454</td>
</tr>
<tr>
<td><strong>Goodness of fit on F²</strong></td>
<td>1.053</td>
<td>1.056</td>
<td>1.104</td>
</tr>
<tr>
<td><strong>R indices [I&gt;2σ(I)]</strong></td>
<td>R₁ = 0.0369, wR₂ = 0.0889</td>
<td>R₁ = 0.0288, wR₂ = 0.0719</td>
<td>R₁ = 0.0377, wR₂ = 0.0784</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R₁ = 0.0457, wR₂ = 0.0929</td>
<td>R₁ = 0.0375, wR₂ = 0.0767</td>
<td>R₁ = 0.0493, wR₂ = 0.0829</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole (e.Å⁻³)</strong></td>
<td>0.353 and -0.379</td>
<td>1.973 and -1.820</td>
<td>3.201 and -1.701</td>
</tr>
</tbody>
</table>
Full crystallographic structure details for complexes 4b and 9b may be obtained in electronic \textit{CIF} format from the Cambridge Crystallographic Data Centre as CCDC 967603 and CCDC 967604 respectively.

\textbf{Table S2.} Crystal data for complexes 4b and 9b.

<table>
<thead>
<tr>
<th></th>
<th>4b</th>
<th>9b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{20}$H$</em>{13}$O$_{9}$PW</td>
<td>C$<em>{40}$H$</em>{26}$Cl$_{18}$P$_2$PtW$_2$</td>
</tr>
<tr>
<td>Formula weight (g/mol)</td>
<td>613.13</td>
<td>1490.24</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>Colour</td>
<td>Red</td>
<td>Red-black</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$C2/c$</td>
<td>$P2_1/n$</td>
</tr>
<tr>
<td>Unit cell dimensions (Å, °)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>40.3819(18)</td>
<td>12.209(3)</td>
</tr>
<tr>
<td>$b$</td>
<td>7.6045(3)</td>
<td>10.307(3)</td>
</tr>
<tr>
<td>$c$</td>
<td>13.7313(6)</td>
<td>37.771(11)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$</td>
<td>93.651(3)</td>
<td>97.669(5)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>4208.1(3)</td>
<td>4170(2)</td>
</tr>
<tr>
<td>$Z$</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated) (Mg/m$^3$)</td>
<td>1.932</td>
<td>2.101</td>
</tr>
<tr>
<td>Absorption coefficient (mm$^{-1}$)</td>
<td>5.616</td>
<td>8.088</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>2360</td>
<td>2800</td>
</tr>
<tr>
<td>Crystal size (mm$^3$)</td>
<td>0.264 x 0.088 x 0.071</td>
<td>0.445 x 0.166 x 0.052</td>
</tr>
<tr>
<td>$\theta$ range for data collection</td>
<td>2.726 to 36.317</td>
<td>2.049 to 28.697</td>
</tr>
<tr>
<td>Index ranges</td>
<td>$h$ -67 to 67</td>
<td>$h$ -16 to 16</td>
</tr>
<tr>
<td></td>
<td>$k$ -12 to 12</td>
<td>$k$ -13 to 13</td>
</tr>
<tr>
<td></td>
<td>$l$ -22 to 22</td>
<td>$l$ -51 to 51</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>153596</td>
<td>131301</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>10217 [R(int) = 0.0548]</td>
<td>12011 [R(int) = 0.0816]</td>
</tr>
<tr>
<td>Completeness to $\theta = 25.242^\circ$</td>
<td>99.90%</td>
<td>99.30%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least squares on $F^2$</td>
<td>Full-matrix least squares on $F^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>10217 / 0 / 281</td>
<td>12011 / 558 / 599</td>
</tr>
<tr>
<td>Goodness of fit on $F^2$</td>
<td>1.112</td>
<td>1.044</td>
</tr>
<tr>
<td>$R$ indices [$I \geq 2\sigma(I)$]</td>
<td>$R1 = 0.0231$, $wR2 = 0.0506$</td>
<td>$R1 = 0.0385$, $wR2 = 0.0714$</td>
</tr>
<tr>
<td>$R$ indices (all data)</td>
<td>$R1 = 0.0342$, $wR2 = 0.0541$</td>
<td>$R1 = 0.0667$, $wR2 = 0.0790$</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e.Å$^3$)</td>
<td>2.425 and -0.606</td>
<td>2.120 and -1.079</td>
</tr>
</tbody>
</table>
References