

Roles Played by Carbene Substituents During Ligand Transfer Reactions Between Tungsten Fischer Carbene Complexes and [Pt(COD)Cl₂]

Nora-ann Weststrate,^a Christopher Hassenrück^b, David C. Liles,^a Simon Lotz,^{*,a} Helmar Görls,^c Rainer F. Winter^{*,b}

^a Department of Chemistry, University of Pretoria, Pretoria, 0002, South Africa

^b Fachbereich Chemie, Universität Konstanz, Konstanz, 78457, Germany

^c Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, Jena, 07743, Germany

**Corresponding Author*

RW: rainer.winter@uni-konstanz.de

ORCID

Rainer Winter: 0000-0001-8381-0647

Simon Lotz: 0000-0002-5313-616X

Nora-ann Weststrate: 0000-0003-0393-2973

Highlights

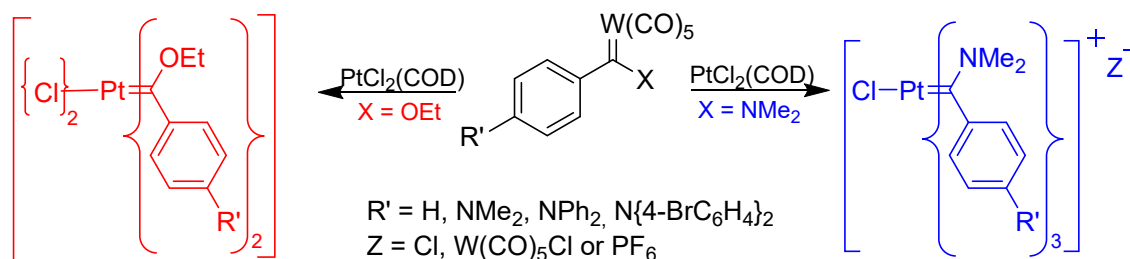
- Bis- and tris(carbene) Pt(II) complexes are made via carbene transfer from W.
- The number of transferable carbene ligands depends on the heteroatom substituent X.
- Remote NR₂ donors impact the electronic properties of carbene ligands.
- Spectroelectrochemistry identifies the remote NR₂ donor as the oxidation site.

Abstract

Fischer carbene ligand transfer reactions from [W{C(X)(C₆H₄-4-R)}(CO)₅] (X = OEt: **a** series; X = NMe₂: **b** series), containing remote tertiary amino substituents R = R'₂N at the phenyl ring, to platinum(II) of [Pt(COD)Cl₂] precursors, are studied. The number of carbene ligands transferred per platinum ion in these cases are determined by the electronic and steric properties of the heteroatoms of the carbene ligand. Thus, neutral bis(carbene) complexes, [Pt{C(X)(C₆H₄-4-R)}₂Cl₂], (R=H (**1a**); R=NR'₂ and R'= Me (**2a**), Ph (**3a**) and 4-BrC₆H₄ (**4a**)), are formed from the ethoxycarbene precursors (X = OEt), while cationic tris(carbene) complexes [Pt{C(X)(C₆H₄-4-R)}₃Cl]⁺ Z⁻, (R=H (**1b**) and R=NR'₂ and R'= (Me (**2b**), Ph (**3b**))

and 4-BrC₆H₄ (**4b**)) are obtained from the aminocarbene precursors (X = NMe₂), the latter with different counter ions Z⁻ = Cl⁻, [W(CO)₅Cl]⁻ or PF₆⁻. Electro- and spectroelectrochemical studies indicate consecutive oxidations of the individual carbene ligands, but also a lack of electronic interactions across the (X)C=Pt=C(X) linkages.

Graphical abstract



The number of carbene ligands transferred from a tungsten carbene precursor to the platinum(II) centre depends on the electronic properties of the carbene substituents at the tungsten atom.

Introduction

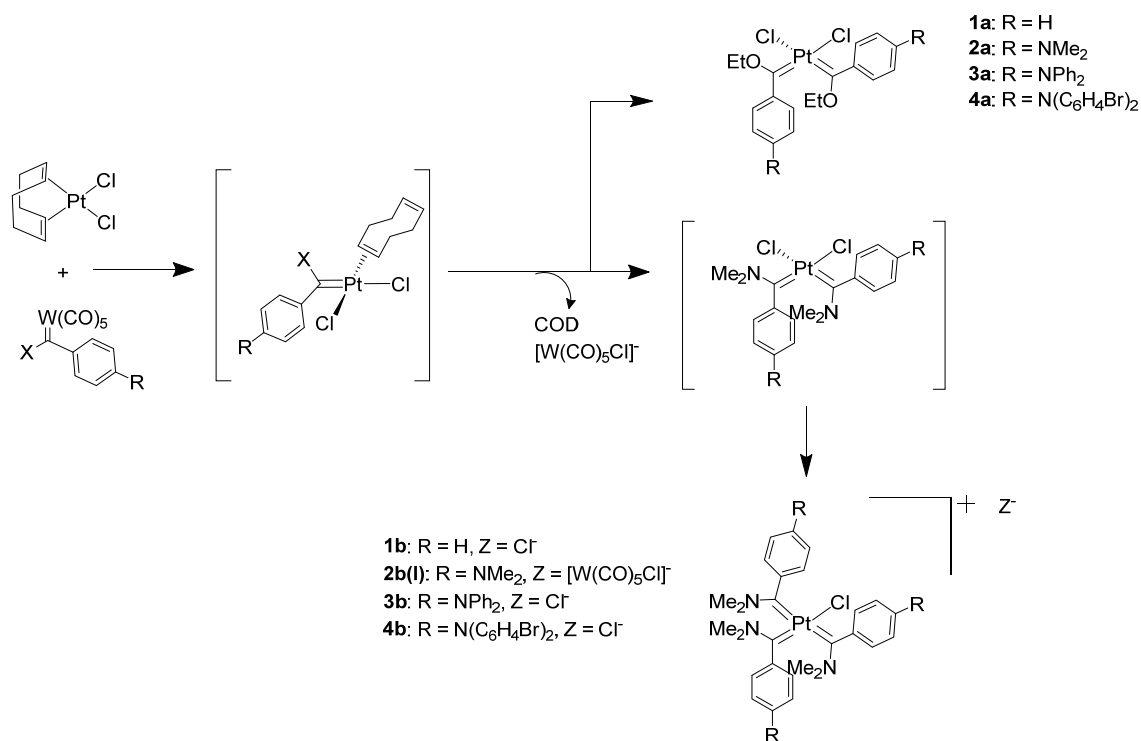
The transfer of a carbene ligand from {M(CO)₅} fragments to other {ML_n} entities has been observed early in Fischer carbene (FC) chemistry.[1–3] Such carbene transfer reactions have meanwhile become a useful means to meet the challenges associated with the synthesis of late transition metal FC complexes,[4,5] and several Pt(II) mono- and bis(carbene) complexes were prepared in this manner.[6–8] The surge for Pt(II) bis(carbene) complexes was partly driven by the objective to trap key intermediates of the well-known self-dimerization reactions of coordinated carbene ligands in the presence of Pd(0) and Pd(II) species.[9,10] Also, the transmetalation of a carbene ligand from a group 6 transition metal to another catalytically active metal fragment are widely applied in organic synthesis.[11] During such studies it was observed that N-heterocyclic carbene ligands (NHC's) are also prone to carbene transfer reactions, sometimes leading to multiple transfers.[12–16]

Recently FC complexes [W{C(X)(C₆H₄-4-R)}(CO)₅] (X = OEt: **a** series; X = NMe₂: **b** series) were synthesized in our laboratories from phenyl substrates containing remote tertiary amino substituents.[17–19] In addition, [W{C(X)(C₆H₅)}(CO)₅] (**a,b**), were also synthesized to aid as reference complexes to probe the effects and magnitude of electron donation by remote tertiary nitrogen substituents. The importance of π -resonance effects within carbene

substituents is an emerging area of research and aims at fine-tuning of the extent of electron donation and the distribution of electron density in the FC carbene ligand.[16,19-21] With the above tungsten complexes of particularly electron-rich ethoxy- and dimethylaminocarbene ligands available, we now set out to probe and study their transferability to Pt(II) precursors.

Results and Discussion

Our synthesis of the Pt(II) carbene complexes involves the substitution of the labile COD (COD = cycloocta-1,5-diene) ligand in [Pt(COD)Cl₂] by the ethoxy- or dimethylaminocarbene ligands of the corresponding tungsten carbene precursors in refluxing dichloromethane to give complexes **1a–4a** and **1b–4b** (Scheme 1). Sierra and co-workers already synthesized bis(ethoxycarbene) complexes of Pt(II) by *transmetallation* reactions from Group 6 transition metal precursors.[22] The ethoxycarbene ligand in these neutral complexes was stabilized by the coordination of a remote nitrogen atom, thus forming five-membered chelate rings. Neutral, acyclic bis(carbene) complexes [Pt{C(OMe)R}₂Cl₂] (R=alkyl), were reported earlier and formed by refluxing hexachloroplatinic acid in butanol with trimethylsilyl-substituted alkynes.[23] In the synthesis of **1a,b - 4a,b**, reaction times of >24 h were applied, depending on the size of the carbene ligand. Bulkier ligands generally require longer reaction times in order to drive the reaction to completion. This is particularly important as the presence of unreacted [Pt(COD)Cl₂] adds to the difficulties encountered during product purification that result from the generally low solubilities of the target complexes and the failure of column chromatographic separation. However, pure complexes are accessible by repeated crystallisations. All products are brown-yellow solids, giving rise to yellow-black appearances of their saturated solutions.



Scheme 1. Synthesis of mononuclear Fischer multicarbene complexes.

The major products formed from tungsten ethoxycarbene precursors are the neutral bis(carbene) complexes **1a–4a**, while aminocarbene precursors behave distinctly different. In these cases, the intermediate bis(aminocarbene) complexes are more reactive and convert to the cationic tris(carbene) complexes **1b–4b**. This contrasts with the behaviour of amino-substituted thienyl and condensed thieno-[2,3-*b*]thienylene carbene ligands, which also afforded bis(aminocarbene) complexes of Pt(II).[24] Even when an excess of [W{C(OEt)(C₆H₄-4-NMe₂)}(CO)₅] and prolonged reaction times were employed, no corresponding cationic tris(ethoxycarbene) complex was isolated. We ascribe the difference to a stronger *trans* influence of the aminocarbene ligands in the Pt(II) cis-configured bis(carbene) complexes, which aids in weakening the *trans* Pt–Cl bond. This would place the ethoxycarbene ligand below the aminocarbene ligand with respect to their *trans* effects. Further substitution of the remaining chloro ligand in cationic complexes **1b–4b** by an aminocarbene ligand to generate a Pt(II) tetra(carbene) complex is likely prevented by steric congestion, as it is evident from the X-ray structure of **2b** (*vide infra*). A NHC-type Pt(II) tetra(carbene) complex was nevertheless isolated by Hahn and co-workers, but in this example the carbene ligands are more rigid and less bulky.[7,25,26]

While all complexes proved to be light-sensitive, the Pt(II) ethoxycarbene complexes are generally more prone to decomposition on prolonged exposure to light. This is particularly true for complex **1a** where the reaction mixture gradually evolved into a suspension of black particles, indicating excessive decomposition. This added to the general difficulties in obtaining pure samples of the complexes and prevented us from obtaining sufficiently pure sample of **1a** for spectroscopic identification. Unlike **1a**, complex **2a** is far more stable, highlighting a supportive electronic donor role played by the remote NMe₂ substituent in **2a**, as was the case for [W(CO)₅{C(OEt)(4-C₆H₄-NMe₂)}], whereby electron density is donated on demand via the phenylene linker to the electrophilic carbene carbon.[19]

The cationic tris(carbene) complexes have Cl⁻ or [W(CO)₅Cl]⁻ as the counter ions, which can readily be exchanged for PF₆⁻ (see Experimental section). The [W(CO)₅Cl]⁻ anion results from the release of a chloro ligand from Pt(II) on substitution with the third carbene ligand and its subsequent reaction with the resulting, coordinatively unsaturated {W(CO)₅} fragment. The presence of the [W(CO)₅Cl]⁻ anion was confirmed by IR and ¹³C NMR spectroscopy as well as by the X-ray structure determination of complex **2b(I)** (see Figure 1 and Figures S1 and S5 of the SI).

Table 1. Selected ¹H and ¹³C NMR resonance signals of the complexes **2a**, **4a** and **2b**, **4b** in CD₂Cl₂.^a

a: X = OEt
b: X = NMe₂
2a,b: R' = NMe₂
4a,b: R' = N(C₆H₄Br)₂

¹ H/ ¹³ C		X = OEt(a)							
		C1	C2	C3	C4	C5	C1OCH ₂ -	OCH ₂ Me	C5NMe ₂
2a	L	/238.5	/156.1	8.41/137.4	6.60/110.8	132.7	5.38/77.5	1.47/14.7	3.11/40.5
4a	L	/n.o.	/157.0	7.58/133.1	7.28/129.9	144.3	5.02(br)/79.7	1.69/14.3	
	L'		/154.5	7.51/129.1	7.13/126.1	143.2	5.02(br)/79.7	1.53/14.1	
¹ H/ ¹³ C		X = NMe ₂ (b)							
		C1	C2	C3	C4	C5	C1NMe ₂		CNMe ₂
2b^b	L, L*	/191.8	/151.1(b)	7.07/126.0	6.73/112.0	125.9	3.87, 3.26/53.3, 44.9		3.87, 3.26/40.5
4b	L	/203.0	/149.8	7.41/127.5	7.09/121.6	146.2	3.70, 3.49/52.3, 49.7		
	L*	/213.1	/155.7	7.17/127.4	6.98/123.0	147.8	4.20, 3.13/46.7, 44.7		

^aSignals indications: not observed (n.o.) and broad (br). ^bDue to broadening of the resonances and to poor resolution no distinctions between ligands L, L* are possible.

Selected ¹H NMR and ¹³C NMR chemical shifts of complexes **2a**, **4a** and **2b**, **4b** are listed in Table 1 (see the Experimental Section for chemical shift assignments of all the complexes as

well as Table S1 and Figures S2 to S7 of the SI). Whereas well-resolved and assignable peaks are observed for **2a** and **2b** in the phenyl region, this is not the case for the ¹H NMR spectra of specifically the bulky aminocarbene complexes **3a,b** and **4a,b**. Poor resolution of peaks for complexes of the **b**-series are ascribed to the large number of overlapping proton resonances in the aromatic region, restricted rotations of bulky substituents (L,L') and the particularly low solubilities. The tris(carbene) complexes feature two kinds of chemically and magnetically different carbene ligands. The one denoted as L represents the singular carbene ligand situated opposite a chloro ligand, while ligands L* are mutually *trans*-disposed to each other (see header of Table 1). Complex **2a**, due to the absence of sterically demanding carbene ligands, displays two well resolved doublets for the aromatic protons of the phenylene ring. In **2b(I)** with the [W(CO)₅Cl]⁻ counter anion, the peak of the *o*-protons is slightly broadened, but the doublet (6.73 ppm, d, *J* = 7.4 Hz) is still assignable with no distinction between ligands L and L*. The slightly broadened methyl resonances of the chemically different dimethylaminocarbene substituents (3.87 and 3.26 ppm) are shifted downfield compared to the single peak of the remote NMe₂ substituent at the phenyl residue (3.01 ppm). The ¹H NMR spectrum of **4a** displays four doublets accounting for the protons of the two phenylene rings and four doublets for the protons of the nitrogen-bonded C₆H₄Br substituents. The duplication of all phenylene resonances into two sets suggest that the two bulky carbene ligands adopt different conformations (L and L') around the Pt(II) coordination plane. The shift difference Δδ of 1.81 ppm for the phenylene protons (*o*- vs *m*-positions) in **2a** indicates that the remote aromatic substituent of the ethoxycarbene ligand {C(OEt)(C₆H₄-4-NMe₂)} is heavily involved in the stabilisation of the electrophilic carbene carbon atom. These shift differences are strongly attenuated in complex **4a** (Δδ = 0.30, 0.38 ppm) with the poorer remote N(*p*-C₆H₄Br)₂ donor substituent at the phenyl ring. The latter approaches the Δδ values in the cationic tris(aminocarbene) complexes (Δδ = 0.30 ppm for **2b** and **4b**), where electron donation from the remote substituent is irrelevant.[19,24]

The ¹³C resonance of the carbene carbon atom of the ethoxycarbene ligand of **2a** appears at 238.5 ppm (*J*_{PtC} = 664 Hz). While similar values of 235.2 and 233.2 ppm were reported for *cis*-[Pt{C(OEt)(R)}₂Cl₂], for R = thienyl and thienothienylene, respectively,[24] the methoxyalkylidene Pt(II) complexes of Steinborn and co-workers, *cis*-[Pt{C(OMe)(R)}₂Cl₂] (R = Me, Et, n-Hexyl), have their carbene resonances shifted further downfield, at δ = 271.1 ppm to 277.9 ppm.[23] The significant shift differences in the case of the present Pt(II) bis(ethoxycarbene) complex **2a** are ascribed to electronic stabilization of the carbene centre by

electron donation from the remote dimethylamino substituent via the conjugated phenylene linker. In the case of the thienyl substituents, the large shift is ascribed to π -resonance effects of the electron excessive thienyl substituents via a conjugated electronic pathway.[24] The chemical shift of the carbene carbon in **2a** (238.5 ppm) is however still downfield compared to that of 191.8 ppm in the tris(dimethylaminocarbene) complex **2b**, where the NMe₂ substituent which is directly attached to the carbene carbon acts as the primary electron donor. This is also borne out by the consistent observation of two separate proton resonances for the *N*-methyl groups for the carbene-bonded NMe₂ substituent, thereby indicating a partial C=N double bond character for complexes of the **b**-series.[19] The ¹³C NMR spectra of the tris(dimethylaminocarbene) complex in **4b** display two carbene resonances, one at 213.1 ppm for the unique carbene L, and one at 203.0 ppm for ligands L*. Their shift to lower field as compared to complex **2b** signals that the identity of the remote donor at the phenyl substituent still retains some influence. The downfield shifts of the carbene resonances in complexes **2b** and **4b** are however clearly surpassed by those of 141.3 ppm and 161.6 ppm for the cationic tris(carbene) complex [Pt(NHC)₃Cl]⁺ (NHC = 1,3-dimethylimidazole-2-ylidene).[7,25,26]

The results of high resolution mass spectrometry (Figures S8 – S13 of the SI) and elemental analysis (see Experimental Section and listed in Table S1 of the SI) support of the NMR-derived identities of the Pt-carbene complexes. For all the aminocarbene complexes of the **b**-series the M⁺ ion peaks were observed, probably indicating reduced reactivity of the ligands in these complexes. By contrast, the ethoxycarbene complexes display molecular ions that are less stable during mass measurements and appear as the M⁺ with or without additional atoms. Examples are [M+Na]⁺ for **2a** and **4a**, and [M-Cl]⁺ for **3a**.

Further confirmation as to the complexes' identities comes from X-ray crystallography. Suitable single crystals of **2a** and **2b**, the latter with either [W(CO)₅Cl]⁻ (**2b(I)**) or PF₆⁻ (**2b(II)**) as the counter anion, were obtained by slow diffusion of *n*-hexane into a saturated solution of the respective complex in CH₂Cl₂ (see Table S2 of the SI for crystallographic details). The molecular structures of **2a**, **2b(I)** and **2b(II)** are shown in Figure 1 and Figures S14 and S15 of the SI, respectively. Selected bond parameters are compiled in Table 2.

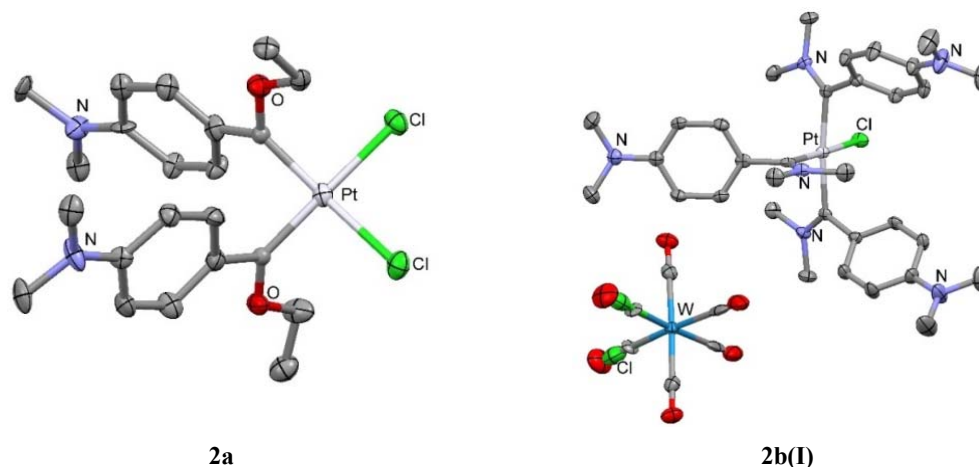
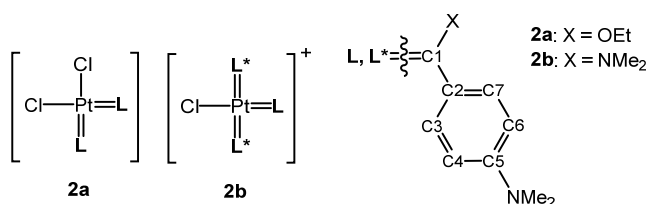


Figure 1. Solid state structures of **2a** and **2b** with $[\text{W}(\text{CO})_5\text{Cl}]^-$ (**2b(I)**) and PF_6^- (**2b(II)**, SI) counter ions. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. **2b(I)** display a disorder of the Cl that can be found in one of two possible positions in the anion $[\text{W}(\text{CO})_5\text{Cl}]^-$

In **2a** the PtC_2 plane defined by the square planar $\text{Pt}(\text{II})$ ion and the two Pt-bonded C atoms of the *cis*-disposed carbene ligands and the PtCl_2 plane containing the two chloro ligands form an angle of 12.72° (S14, SI). The carbene ligands are arranged such that the ethoxy and the phenyl substituents are found on opposite sides of the coordination plane. As in $[\text{W}\{\text{C}(\text{OEt})(\text{C}_6\text{H}_4\text{-4-NMe}_2)\}(\text{CO})_5]$, both carbene ligands in **2a** are fully planar.[19] This planarity adds structural evidence to the conclusions derived from the NMR data that the 4-Me₂N-C₆H₄ substituents are π -conjugated with the carbene carbon atoms of **2a**. The two planes through the carbene ligands form angles of 71.1° and 65.3° with the $\text{Pt}(\text{II})$ coordination plane. The Pt–C distances of 1.934(14) and 1.938(14) Å in complex **2a** fall close to those of 1.932(7) to 1.965(7) Å for the related bis(methoxycarbene) complexes $[\text{Pt}\{\text{C}(\text{OMe})(\text{R})\}_2\text{Cl}_2]$ (R = Me, Et).[23] In the crystalline state, the two chloro ligands of **2a** engage in hydrogen bonding to methyl protons of two different C₆H₄-4-NMe₂ substituents with CH \cdots Cl contacts of 2.783 Å to 2.912 Å, or with a phenylene proton α to the NMe₂ substituent ($d(\text{CH}\cdots\text{Cl}) = 2.778$ Å). Further details as well as graphical representations of the packing motifs and H-bond interactions can be found in the SI (see Figure S17 and the discussion there).

In both structures of **2b**, the $\text{Pt}(\text{II})$ ion is in a slightly distorted, square planar environment and is coordinated to one chloro and three carbene ligands (see Figure S15 of the SI). The aryl substituents of the carbene ligands are alternately oriented to above or below the coordination plane. Crucial bond parameters of the two symmetry-equivalent, *trans*-disposed carbene ligands (denoted as L* in Table 2) and the unique carbene ligand *trans* to the chloro ligand (denoted as L) show consistent differences in both structures. Firstly, the C₆H₄-4-NMe₂ ring

of the L ligand adopts a near orthogonal orientation with respect to the coordination plane, while those of the L* ligands are with *ca.* 45° in an orientation between orthogonal and coplanar. Secondly, the Pt–C1 bond lengths to the individual carbene ligands respond to the differing *trans* influences of the chloro and the carbene ligands. A detailed comparison of bond distances can be found as Figure S16 of the SI. Thus, the Pt–C distances to the mutually *trans*-disposed ligands L* fall in a narrow range of 2.051(4) to 2.059(4) and are by 0.08 Å longer than those of 1.975(6) Å or 1.973(4) Å to the ligand L. Similar Pt–C1 bond lengths of 2.064(7) Å, 2.038(7) Å and 1.989(7) Å were observed in a NHC Pt(II) tris(carbene) complex.[27] Both structures also exhibit highly aesthetic intermolecular packing motifs and intricate hydrogen-bonding networks. Details can be found in the SI along with graphical displays (see Figures S18, S19). The large separations of 6.210 Å (**2a**), 8.979 Å (**2b(I)**) and 8.031 Å (**2b(II)**) between Pt ions of adjacent molecules rule out any Pt···Pt interactions in the solid state.[28]

Table 2. Selected bond lengths, bond angles and torsion angles of **2a**, **2b(I)** and **2b(II)**.

	2a	2b(I)^a		2b(II)	
	L	L*	L	L*	L
Bond lengths					
Pt–C1	1.934(14), 1.938(14)	2.053(4)	1.975(6)	2.059(4), 2.051(4)	1.973(4)
C1–O(Et)	1.341(17), 1.304(16)	-	-	-	-
C1–N	-	1.311(5)	1.318(8)	1.308(5), 1.302(5)	1.307(5)
C1–C2	1.442(19), 1.487(19)	1.490(6)	1.473(9)	1.462(6), 1.487(6)	1.494(5)
Pt–Cl	2.389(4) 2.377(4)	2.380(2)		2.380(1)	
N–C4	1.366(18)	1.382(6)	1.376(9)	1.368(5), 1.382(6)	1.385(6)
Bond angles					
O/N–C1–C2	109.8(12), 108.3(12)	119.7(4)	116.6(6)	119.5(4), 118.2(4)	117.4(3)
Pt–C1–O/N	120.6(10), 124.5 (10)	124.3(3)	125.5(5)	118.1(3), 124.4(3)	125.2(3)
Pt–C1–C2	129.5(10), 126.9 (9)	116.0(3)	117.9(4)	118.1(5), 117.4(3)	117.4(3)
C1–Pt–C1'	90.3(6)	91.09(11)	91.09(11)	173.21(15)	90.15(16), 95.03(16)
Torsion angles					
Pt–C1–C2–C3	-16(2) -2(2)	47.8(5)	92.0(5)	44.5(5)	-71.1(4)
O/N–C1–C2–C7	-8.5(2)	56.2(6)	88.0(5)	48.4(6)	-70.3(5)
C–N–C5–C4	-6.0(7)	5.3(9)	14.1(8)	4.2(9)	16.7(7)

^a In the case of **2b(I)**, the two L* ligands are related by mirror symmetry. L is the symbol used for a carbene ligand *trans* to a chloro ligand and L* for a carbene ligand *trans* to a carbene ligand.

Cyclic voltammetry studies showed the neutral bis(carbene) and cationic tris(carbene) platinum complexes to be electroactive. Graphical accounts of their CVs are included as Figures S20 to S26 of the SI, while relevant data are collected in Table 3. One irreversible reduction wave was observed for every diarylamine-appended derivative, irrespective of the nature of the heteroatom substituent X at the carbene carbon atom. This process seems to be shifted to outside the accessible potential range in the dimethylaniline-substituted congeners **1a,b**. More interesting is the observation of one or more oxidations, which become at least partially

reversible for the triarylamine-appended complexes, with either phenyl (**3a,b**) or 4'-bromophenyl (**4a,b**) substituents R'. Of particular note is the finding that the half-wave or peak potentials of the cationic tris(aminocarbene) complexes are consistently lower than those of their neutral bis(ethoxycarbene) congeners. This shows that electron donation from the NMe₂ substituent even outweighs the presence of a third carbene ligand and of an outer, unipositive charge. The strong anodic shifts of the half-wave potentials between the pairs of complexes **3a/4a** and **3b/4b** as well as the presence two consecutive waves in the case of complexes **3a,b** and **4a** provide a first, strong argument that the oxidation of these complexes is based on the triarylamine-type moieties of the individual carbene ligands rather than on the platinum centre or the carbene moiety itself. The same probably holds for the dimethylaniline derivative **2b**, where even three consecutive, however chemically irreversible, anodic peaks are observed. This nevertheless signals that all three carbene ligands are independently oxidized. Obviously, in this particular environment, delocalization of the positive charge onto the periphery of the redox-active 4-R'₂N-C₆H₄- subunits is required in order to chemically stabilize the corresponding oxidized forms. Complex **2a** seems to be an outlier with a more metal-based oxidation, as indicated by its much higher first oxidation potential.

Table 3. Oxidation and reduction half wave potentials (V) of **2a** – **4a** and **2b** – **4b** in CH₂Cl₂ / 0.1 M NBu₄PF₆ at a scan rate of 100 mV/s

Complex	E^{ox} / V	E^{red} / V	Complex	E^{ox} / V	E^{red} / V
2a	0.950 ^a , 1.080 ^a	n. o.	2b	0.175 ^a , 0.330 ^a , 0.665 ^a	n. o.
3a	0.520, 0.930	-2.400 ^a	3b	0.390, 0.550	-2.360 ^a
4a	0.970	-2.270 ^a	4b	0.680	-2.220 ^a

^aPeak potential of a chemically irreversible process.

In order to experimentally probe the above conclusion about the identity of the primary redox site in the triarylamine-type complexes, we electrochemically oxidized complex **4b**, which is the only complex of this series whose oxidized form is sufficiently stable on the timescale of the CV experiment. Bulk electrolysis while continuously monitoring the evolution of UV/Vis/NIR spectra resulted in the growth of a structured band at 714 nm, which, in terms of its position and shape, can be viewed as characteristic of a triphenylaminium cation (Figure 2).[29–32] The well-defined isosbestic point and the optical recovery of the starting spectra on potential reversal attest to chemical stability of the oxidized form on also the longer timescale of electrolysis. The absence of any additional NIR intervalence charge-transfer (IVCT) band at any point of the electrolysis argues against electronic coupling between the remote triarylaminium sites of individual ligands. Contrasting cases are provided by the complex *trans*-[Pt(PEt₃)₂{-CC-C₆H₄N(C₆H₄-4-OMe)₂}₂], whose one-electron oxidized form exhibits

an IVCT band at 1530 nm (6540 cm^{-1}),[33] and a one-electron oxidized A-frame diplatinum complex carrying two axial redox-active ferrocenylethynyl ligands.[34]

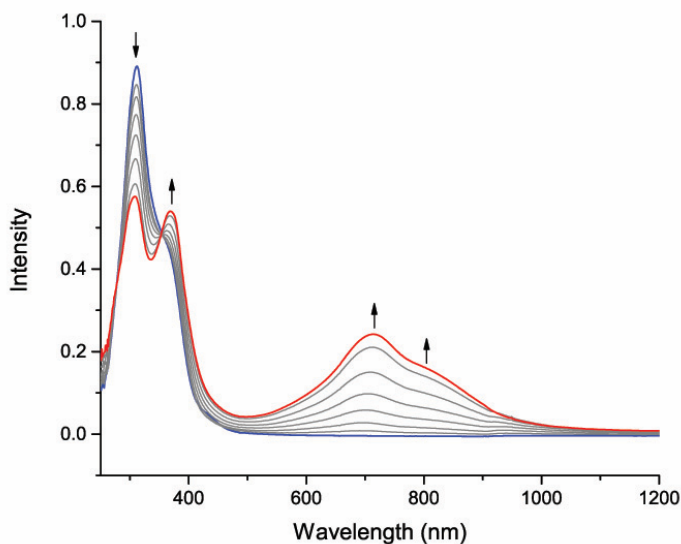


Figure 2. Spectroscopic changes during the one-electron oxidation of complex **4b** in 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ / 0.1 M NBu_4PF_6 .

Experimental

Material and Methods

Standard Schlenk techniques, under an atmosphere of Ar or N_2 were used for synthesis. THF and *n*-hexane were distilled over sodium metal, while CH_2Cl_2 was distilled over CaH_2 . All other reagents were used as received from commercial suppliers. Et_3OBF_4 was synthesised according to the published procedure by Meerwein.[35] The aminolysis with dimethylamine of the compounds is achieved through an acid-base reaction between dimethylammonium chloride and sodium hydroxide in an aqueous environment.[36] The *in situ* formed HNMe_2 aminolyses the ethoxycarbene and illustrates a convenient method to generate dimethylaminocarbene complexes from ethoxycarbene complexes, comparable to the widely used bubbling of ammonia through an ether solution of any ethoxycarbene complex.[37] The precursors, $[\text{W}(\text{CO})_5\{\text{C}(\text{X})p\text{-C}_6\text{H}_4\text{NR}\}]$ X=OEt (**a**), NMe_2 (**b**), R=H(**1'**), NMe_2 (**2'**), NPh_2 (**3'**) and $\text{N}(\text{C}_6\text{H}_4\text{Br})_2$ (**4'**), were synthesised according to the literature.[19] Silica gel 60 (particle size 0.0063–0.200 mm) was used as resin for all separations in column chromatography. NMR spectra were recorded on Bruker Ultrashield Plus 400 AVANCE 3 and Bruker Ultrashield 300 AVANCE 3 spectrometers using CD_2Cl_2 as solvent at 25 °C. The NMR spectra were recorded for ^1H at 400.13 or 300.13 MHz and ^{13}C at 100.163 or 75.468 MHz. Chemical shifts were

recorded in ppm, using the residual signal of the protonated solvent as an internal reference. For CD₂Cl₂ δH at 5.3400 and δC at 53.840 ppm. Cyclic voltammetry was performed in an air-tight, one compartment cell with a Pt working electrode (1.6 cm diameter from BAS), a Pt counter electrode and an Ag wire as reference electrode. Before measurements, the working electrode was polished with 1 μm and 0.25 μm diamond pastes (Buehler-Wirtz). NBu₄PF₆ (0.25 mM) was used as the supporting electrolyte in CH₂Cl₂. Referencing was done with addition of ferrocene as an internal standard to the analyte solution after all data of interest had been acquired. Representative sets of scans were repeated with the added standard. Final referencing was done against the ferrocene/ferrocenium (Cp₂Fe^{0/+}), whose potential is set as 0 mV. A custom-built optically transparent thin layer electrolysis cell equipped with CaF₂ windows, Pt mesh as working and counter electrodes and a thin Ag sheet as the pseudo-reference electrode following the design of Hartl and co-workers was used in the UV/Vis/NIR spectroelectrochemical experiment.[38]

Crystallography

The intensity data for compounds **2a**, **2b(I)** and **2b(II)** were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-*K*α radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.[39–41]

The structures were solved by direct methods using *SHELXS*[42] and refined by full-matrix least squares techniques against Fo² using *SHELXL-97*.[43] The hydrogen atoms of compound **2a** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters.

The crystal of **2a** was a non-merohedral twin. The twin law was determined by *PLATON*[44] to be (0.003 0.997 0.000) (1.003 -0.003 0.000) (0.000 0.000 -1.000). The contribution of the main component was refined to 0.845(1).

Synthesis and characterization of platinum(II) carbene complexes via carbene transfer reactions (2a - 4a, 1b - 4b)

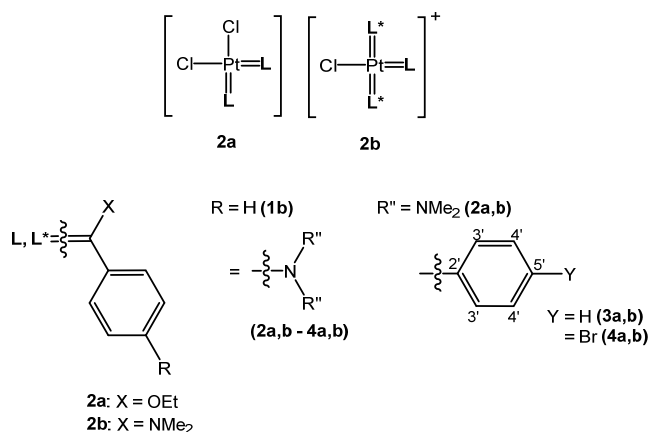


Figure 3. NMR positional assignments for complexes **2a** – **4a** and **1b** – **4b**.

Method: An excess (n mmol) of a specific tungsten carbene complex [14] and m mmol of [Pt(COD)Cl₂] (see Table 4) were dissolved in 20 ml dried dichloromethane and allowed to stir under an inert atmosphere at 50 °C for 24 to 30 hours. The solvent was evaporated, and the reaction residue dissolved in a minimal amount of dichloromethane. The product was cannula filtered and triturated into *n*-hexane (for ethoxycarbene complexes) or diethyl ether (for aminocarbene complexes) and repeatedly washed with the same solvent until the solvent remained colourless. The product was dried under vacuum and fully characterized after (repeated) crystallisation. Experimental data for the synthesis of the individual complexes are recorded in Table 4.

Method for exchange of counter anion by PF₆⁻ in cationic triscarbene Pt complexes

The Pt compound (**2b(II)**, 0.1758 g, 0.1572 mmol) and excess KPF₆ was dissolved in CH₂Cl₂ to form a dark yellow solution. The solution was allowed to stir for 20 hours at room temperature. The resulting product was isolated by trituration into hexane, canula filtration and dried under vacuum. A quantitative yield (0.1392 g, 0.1540 mmol) was obtained.

NMR assignments are reported as per Figure 3.

Table 4. Experimental details of synthetic methods.

Product	W carbene n (mmol)	Pt(COD)Cl ₂ m (mmol)	Reaction time (h)	Yield G
2a	5.91 mmol, (2.96 g)	2.00 mmol, (0.75 g)	30	0.947 (76.3 %)
3a	0.32 mmol, (0.20 g)	0.08 mmol, (0.03 g)	27	0.040 (43 %)
4a	0.60 mmol (0.47 g)	0.18 mmol, (0.067 g)	24	0.125 (58.6 %)
1b	1.66 mmol (0.71 g)	0.75 mmol, (0.281 g)	21	0.159 (32.9%)
2b	6.02 mmol, (2.84 g)	1.63 mmol, (0.611 g)	24	1.347 (73.9 %)
3b	0.32 mmol, (0.20 g)	0.08 mmol, (0.03 g)	27	0.038 (41 %)
4b	0.47 mmol, (0.36 g)	0.12 mmol, (0.043 g)	24	0.179 (93.2 %)

1a: C₂₂H₂₀O₂N₂PtCl₂. The product is unstable and decomposes on light exposure. No unambiguous spectroscopic assignments could be made.

2a: C₂₂H₃₀O₂N₂PtCl₂. ¹H NMR (CD₂Cl₂, 400 MHz) δ 8.41 (d, *J* = 9.2 Hz, 2H, H3), 6.60 (d, *J* = 9.2 Hz, 2H, H4), 5.38 (s, 2H, CH₂ (OEt)), 3.11 (s, 6H, NMe), 1.47 (t, *J* = 7.1 Hz, 3H, CH₃ (OEt)). ¹³C NMR (CD₂Cl₂, 101 MHz) δ 238.5 (C_{carb}, ¹*J*_{PtC} = 664 Hz), 156.1 (C2), 137.4 (C3), 132.7 (C5), 110.8 (C4), 77.5 (CH₂ (OEt)), 40.5 (NMe), 14.7 (CH₃ (OEt)). ESI-MS (2.8eV, positive mode, *m/z*): calcd for [M+H]⁺ 620.1410; found 620.1449.

3a: C₄₂H₃₈O₂N₂PtCl₂. ¹H NMR spectra poorly resolved due to overlapping peaks in the Ph-region and a large noise to peak ratio due to poor solubility in ¹³C NMR spectrum complicated unambiguous peak assignment. ESI-MS (2.8eV, positive mode, *m/z*): calcd for [M-Cl]⁺ 833.2271; found 833.2268. Combustion Analysis: calcd: C: 64.67 %, H: 4.91 %, N: 3.59 %. Found: C: 64.38 %, H: 5.15 %, N: 3.81 %.

4a: C₄₂H₃₄O₂N₂Br₄PtCl₂. ¹H NMR (CD₂Cl₂, 400 MHz) **L(1):** δ 7.58 (d, *J* = 8.5 Hz, 2H, H3), 7.28 (d, *J* = 8.5 Hz, 2H, H4), 7.35 (d, *J* = 8.0 Hz, 4H, H3'), 7.06 (d, *J* = 8.0 Hz, 4H, H4'), **L(2):** 7.51 (d, *J* = 7.9 Hz, 2H, H3) 7.13 (d, *J* = 7.9 Hz, 2H, H4), 7.06, (d, *J* = 7.8 Hz, 4H, H3') 6.97 (d, *J* = 7.8 Hz, 2H, H4'), 5.02 (q, *J* = 7.0 Hz, 4H, CH₂ (OEt)) 1.69, 1.53 (each t, *J* = 7.0 Hz, 6H, CH₃ (OEt)). ¹³C NMR (CD₂Cl₂, 101 MHz) δ n.o. (C_{carb}), 157.0, 154.5 (C2), 147.3, 147.0 (C2'), 144.3, 143.2 (C5), 132.6 (C3'), 125.8 (C4'), 133.1, 129.1 (C3), 129.9, 126.1 (C4) 117.3, 115.6 (C5'), 79.7 (CH₂ (OEt)), 14.3 (CH₃ (OEt)), 14.1 (CH₃ (OEt)). ESI-MS (2.8eV, positive mode, *m/z*): calcd for [M+Na]⁺ 1206.8236; found 1206.8271. Combustion Analysis: calcd C = 42.59 %, H = 2.89 %, N = 2.37 %; found C = 42.67 %, H = 2.99 %, N = 2.47 %.

1b: C₂₇H₃₃N₃PtCl₂. **1b** is more stable than **1a**, but still decomposes on light exposure. ¹H NMR (CD₂Cl₂, 400 MHz) δ 7.52 (d, *J* = 8.4 Hz, 2H, H4(L)), 7.51 (d, *J* = 7.8 Hz, 4H, H4(L*)), 7.41 (d, *J* = 8.4 Hz, 1 H (H5(L)), 7.40 (d, *J* = 7.8 Hz, 2H, H5(L*)), 7.14 (d (br.), *J* = 7.4 Hz, 6H, H3(L,L*)), 3.86 (br.), 3.29 (each 3H, NMeL) 3.56, 3.07 (each 6H, NMeL*). ¹³C NMR (CD₂Cl₂,

101 MHz) δ 217.7 (C_{carb,L^*}), 213.3 ($C_{\text{carb},L}$), 145.2 ($C2L^*$), 144.9 ($C2L$), 129.6-122.0 ($C3$, $C4$ L,L^*), 122.9 ($C5$, L,L^*), 49.6, 44.6 (NCH_3 , L,L^*). ESI-MS (2.8eV, positive mode, m/z): calcd for $[M]^+$ 630.2012; found 630.2158. $[M = C_{27}H_{33}N_3PtCl]^+$

2b(I): $C_{38}H_{48}N_6O_5WPtCl_2$. 1H NMR (CD_2Cl_2 , 400 MHz) δ 7.07 (d, $J = 8.8$ Hz, 6H, $H3(L,L^*)$), 6.73 (d (*br*), $J = 7.4$ Hz, 6H, $H4(L,L^*)$), 3.87 (s (*br*), 9H, $NMe_{\text{carb}}(L,L^*)$), 3.26 (s, 9H, $NMe_{\text{carb}}(L,L^*)$), 3.01 (s, 18H, $NMe_2(L,L^*)$). ^{13}C NMR (CD_2Cl_2 , 101 MHz) δ 202.7 ($[W(CO)_5Cl]^-$, *trans*, $J_{WC} = 13.64$ Hz), 200.1 ($[W(CO)_5Cl]^-$, *cis*, $J_{WC} = 64.6$ Hz), 191.8 ($C_{\text{carb}}(L,L^*)$), 151.2 ($C2(L,L^*)$), 132.7, 124.2 ($C5(L,L^*)$), 126.0 ($C3(L,L^*)$), 112.0 ($C4(L,L^*)$), 53.3 ($C_{\text{carb}}NMeL,L^*$), 44.9 ($C_{\text{carb}}NMeL,L^*$), 40.5 ($NMeL,L^*$). ESI-MS (2.8eV, positive mode, m/z): calcd for $[M = C_{33}H_{48}N_6PtCl]^+$ 759.3278; found 759.3279.

3b: $C_{63}H_{60}N_6PtCl_2$. 1H NMR (CD_2Cl_2 , 300 MHz) δ 7.38 - 7.29 (m, 12H, $H3$, $H3'(L,L^*)$), 7.20 - 7.16 (m, 6H, $H3'(L,L^*)$), 7.16 - 7.05 (d (*br*), 18H, $H3$, $H4'(L,L^*)$), 7.01 - 6.97 (m, 6H, $H5'(L,L^*)$), 4.09 (s, 3H, $NMe(L)$), 3.72 (s, 6H, $NMe(L^*)$), 3.49 (s, 3H, $NMe(L)$), 3.13 (s, 6H, $NMe(L^*)$). ESI-MS (2.8eV, positive mode, m/z): calcd for $[M = C_{63}H_{60}N_6PtCl]^+$ 1131.4217; found 1131.4283. Combustion Analysis: calcd C = 64.83 %, H = 5.18 %, N = 7.43; found C = 64.62%, H = 4.94 %, N = 7.58.

4b: $C_{63}H_{54}N_6Br_6PtCl_2$. 1H NMR (CD_2Cl_2 , 400 MHz) δ 7.46 - 7.41 (m, 12H, $H3$, $H3'$), 7.18 - 7.08 (m, 6H, $H3'$), 7.07 - 6.98 (m, 18H, $H4$, $H4'$), 4.20, 3.49 (2s, 9H, NMe), 3.70, 3.13 (2s, 9H, NMe). ^{13}C NMR (CD_2Cl_2 , 101 MHz) δ 213.1 ($C_{\text{carb}}(L^*)$), 203.0 ($C_{\text{carb}}(L)$), 155.7 ($C2(L^*)$), 149.8 ($C2(L)$), 147.8 ($C5(L^*)$), 146.2 ($C2'(L)$), 146.2 ($C5(L)$), 133.3 ($C4'(L^*)$), 133.1, 127.5, 127.4 123.0, 121.6, 117.8, 116.9 ($C3$, $C4$, $C3'$, $C4'$), 52.3 ($NMe(L)$), 49.7 ($NMe(L)$), 46.7 ($NMe(L^*)$), 44.7 ($NMe(L^*)$). ESI-MS (2.8eV, positive mode, m/z): calcd for $[M = C_{63}H_{54}N_6Br_6PtCl]^+$ 1604.8786; found 1604.8789. Combustion Analysis: calcd C = 46.12%, H = 3.32 %, N = 5.13%; found C = 46.01 %, H = 3.34 %, N = 5.35 %.

Conclusions

Based on our results we conclude that oxy- and aminocarbene ligands differ with respect to how many of them can be transferred from the corresponding tungsten carbene complexes to $[Pt(COD)Cl_2]$. Electron donation by the 4-NR'₂-C₆H₄ substituent of the carbene ligands $\{C(OEt)(C_6H_4-4-NR'_2)\}$ does not suffice to promote the substitution of also one chloro ligand, thereby providing only neutral bis(carbene) Pt-complexes, *cis*- $[Pt\{C(OEt)(C_6H_4-4-NR'_2)\}_2Cl_2]$, even in the presence of excess tungsten carbene complexes. By contrast,

aminocarbene ligands allow for replacement of one chloro ligand, thus affording cationic Pt-tris(carbene) complexes. This we ascribe to the larger *trans*-effect of a more electron-rich dimethylaminocarbene ligand, which serves to labilize the chloro ligands in an intermittently formed bis(carbene) complex. The substitution of the remaining chloro ligand is probably impeded by steric congestion around the Pt centre, as is also evident from restricted rotations of the carbene substituents. According to the NMR and IR data as well as the redox properties of the Pt complexes, the differences between coordinated oxy- and aminocarbene ligands of the W-precursors also prevail in the Pt complexes.[19] Remarkably, stronger electron donation from the dimethylaminocarbene as compared to the oxycarbene ligands even outweighs the positive, outer charge. In addition, the presence of the remote 4-NR₂ donor directs the first oxidation of the aminocarbene complexes away from the metal carbene entity to the triarylamine constituent.

Associated Content

Supplementary information (SI) submitted consists of NMR spectra data, High Resolution Mass spectra, infrared spectra, crystallography determined data and cyclic voltammograms. The Supporting Information is available free of charge. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication with deposition numbers CCDC-1917581 for **2a**, CCDC-1917582 for **2b(I)**, and CCDC-1917583 for **2b(II)**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Author contributions

The manuscript was written through contributions of all authors. All authors have approved to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Acknowledgements

The authors acknowledge support by the state of Baden-Württemberg. In addition, SL and NW acknowledge the Alexander von Humboldt Foundation and University of Pretoria for funding

research visits in Konstanz. SL acknowledges the NRF (RSA) for financial support of the project by GUN 87788 and 95772 grants.

References

- [1] E.O. Fischer, H. -J Beck, Transfer of Methoxyphenylcarbene Ligands from Molybdenum to Iron and Nickel, *Angew. Chemie Int. Ed. English*. 9 (1970) 72–73.
- [2] R. Aumann, E.O. Fischer, Neue Gold-Carben-Komplexe durch Carbenübertragung, *Chem. Ber.* 114 (1981) 1853–1857.
- [3] E.O. Fischer, M. Böck, Übergangsmetall-Carben-Komplexe, CXXXVII Darstellung zweikerniger Gold(I)-Biscarben-Komplexe durch Carbenübertragungen von Wolfram auf Gold, *Monatsh. Chem.* 115 (1984) 1159–1164.
- [4] I. Fernández, M.J. Mancheño, R. Vicente, L.A. López, M.A. Sierra, Transmetalation reactions from Fischer carbene complexes to late transition metals: A DFT study, *Chem. - A Eur. J.* 14 (2008) 11222–11230.
- [5] P. Mathew, A. Neels, M. Albrecht, 1,2,3-Triazolylidenes as versatile abnormal carbene ligands for late transition metals, *J. Am. Chem. Soc.* 130 (2008) 13534–13535.
- [6] M. Frøseth, K.A. Netland, C. Rømming, M. Tilset, Synthesis and characterization of novel Pd(II) and Pt(II) complexes with 5-ring chelating iminoylcarbene ligands, *J. Organomet. Chem.* 690 (2005) 6125–6132.
- [7] F.E. Hahn, M.C. Jahnke, T. Pape, Synthesis of palladium and platinum complexes with phosphine-functionalized benzimidazol-2-ylidene ligands, *Organometallics*. 25 (2006) 5927–5936.
- [8] F. Kessler, N. Szesni, C. Maaß, C. Hohberger, B. Weibert, H. Fischer, Transfer of heterocyclic carbene ligands from chromium to gold, palladium and platinum, *J. Organomet. Chem.* 692 (2007) 3005–3018.
- [9] J.C. Del Amo, M.J. Mancheño, M. Gómez-Gallego, M.A. Sierra, Catalytic transmetalation of alkoxychromium(0) carbenes to late transition metals: Self-dimerization and cyclopropanation reactions, *Organometallics*. 23 (2004) 5021–5029.
- [10] R.C. Klet, J.A. Labinger, J.E. Bercaw, Diverse C–C Bond-Forming Reactions of Bis(carbene)platinum(II) Complexes, *Organometallics*. 31 (2012) 6652–6657.
- [11] Mar Gómez-Gallego, and María José Mancheño, M.A. Sierra*, Catalytic Transmetalation from Group 6 Fischer Carbene Complexes: An Emerging Powerful Tool in Organic Synthesis, *Acc. Chem. Res.* 38 (2004) 44–53.
- [12] S.T. Liu, K.R. Reddy, Carbene transfer reactions between transition-metal ions, *Chem.*

- Soc. Rev.* 28 (1999) 315–322.
- [13] I.J.B. Lin, C.S. Vasam, Review of gold(I) N-heterocyclic carbenes, *Can. J. Chem.* 83 (2005) 812–825.
- [14] A.M. Voutchkova, M. Felix, E. Clot, O. Eisenstein, R.H. Crabtree, Imidazolium carboxylates as versatile and selective N-heterocyclic carbene transfer agents: synthesis, mechanism, and applications, *J. Am. Chem. Soc.* 129 (2007) 12834–12846.
- [15] S. Stipurin, T. Strassner* C⁺C* Platinum(II) complexes with electron-withdrawing groups and beneficial auxiliary ligands: Efficient blue phosphorescent emission, *Inorg. Chem.* 60 (2021) 11200–11205
- [16] R. Visbal, M.C. Gimeno, N-heterocyclic carbene metal complexes: photoluminescence and applications, *Chem. Soc. Rev.* 43 (2014) 3551–3574.
- [17] N. Weststrate, I. Fernández, D.C. Liles, N. Van Jaarsveld, S. Lotz, Fischer-type carbene complexes of tris(1,4-phenylene)amines and tri(2-furyl)phosphine, *Organometallics.* 34 (2015) 696–710.
- [18] N. Weststrate, S. Bouwer, C. Hassenrück, N.A. van Jaarsveld, D.C. Liles, R.F. Winter, S. Lotz, Synthesis and properties of Fischer carbene complexes of N,N-dimethylaniline and anisole π -coordinated to chromium tricarbonyl, *J. Organomet. Chem.* 869 (2018) 54–66.
- [19] N. Weststrate, C. Hassenrück, M. Linseis, D.C. Liles, S. Lotz, H. Görls, R.F. Winter, The Effect of Remote Donor Substituents on the Properties of Alkoxy and Amino Fischer Carbene Complexes of Tungsten, *Z. Anorg. Allg. Chem.* (2021).
- [20] G.M. Chu, A. Guerrero-Martínez, C.R. de Arellano, I. Fernández, M.A. Sierra, Remote Control by π -Conjugation of the Emissive Properties of Fischer Carbene-BODIPY Dyads, *Inorg. Chem.* 55 (2016) 2737–2747.
- [21] W. Ruan, C. Shi, H.H.Y. Sung, I.D. Williams, G. Jia, Synthesis and reactivity of platinum vinylcarbene complexes prepared from activation of propargyl alcohols, *J. Organomet. Chem.* 880 (2019) 7–14.
- [22] M.P. López-Alberca, M.J. Mancheño, I. Fernández, M. Gómez-Gallego, M.A. Sierra, R. Torres, Synthesis and properties of mononuclear group 10 alkoxy-biscarbene complexes, *Chem. - A Eur. J.* 15 (2009) 3595–3603.
- [23] M. Werner, T. Lis, C. Bruhn, R. Lindner, D. Steinborn, Synthesis and reactivity of bis(alkoxyalkylidene)platinum(II) complexes, *Organometallics.* 25 (2006) 5946–5954.
- [24] Z. Lamprecht, F.P. Malan, S. Lotz, D.I. Bezuidenhout, Synthesis and structure of

- thienyl Fischer carbene complexes of Pt(II) for application in alkyne hydrosilylation, *New J. Chem.* 45 (2021) 6220–6230.
- [25] F.E. Hahn, V. Langenhahn, T. Pape, Template synthesis of tungsten complexes with saturated N-heterocyclic carbene ligands, *Chem. Commun.* (2005) 5390–5392.
- [26] F.E. Hahn, V. Langenhahn, T. Lügger, T. Pape, D. Le Van, Template synthesis of a coordinated tetracarbene ligand with crown ether topology, *Angew. Chemie - Int. Ed.* 44 (2005) 3759–3763.
- [27] F. Hering, U. Radius, From NHC to Imidazolyl Ligand: Synthesis of Platinum and Palladium Complexes d¹⁰-[M(NHC)₂] (M = Pd, Pt) of the NHC 1,3-Diisopropylimidazolin-2-ylidene, *Organometallics*. 34 (2015) 3236–3245.
- [28] S.W. Lai, M.C.W. Chan, T.C. Cheung, S.M. Peng, C.M. Che, Probing d⁸-d⁸ interactions in luminescent mono- and binuclear cyclometalated platinum(II) complexes of 6-phenyl-2,2'-bipyridines, *Inorg. Chem.* 38 (1999) 4046–4055.
- [29] S. Dapperheld, E. Steckhan, K.G. Brinkhaus, T. Esch, Organic Electron Transfer Systems, II Substituted Triarylamine Cation-Radical Redox Systems – Synthesis, Electrochemical and Spectroscopic Properties, Hammet Behavior, and Suitability as Redox Catalysts, *Chem. Ber.* 124 (1991) 2557–2567.
- [30] R.I. Walter, Substituent Effects on the Properties of Stable Aromatic Free Radicals. The Criterion for Non-Hammett Behavior, *J. Am. Chem. Soc.* 88 (1966) 1923–1930.
- [31] S. Amthor, B. Noller, C. Lambert, UV/Vis/NIR spectral properties of triarylamines and their corresponding radical cations, *Chem. Phys.* 316 (2005) 141–152.
- [32] H. Murata, P.M. Lahti, Synthesis- and oxidation of triarylamine derivatives bearing hydrogen-bonding groups, *J. Org. Chem.* 72 (2007) 4974–4977.
- [33] S.C. Jones, V. Coropceanu, S. Barlow, T. Kinnibrugh, T. Timofeeva, J.L. Brédas, S.R. Marder, Delocalization in platinum-alkynyl systems: A metal-bridged organic mixed-valence compound, *J. Am. Chem. Soc.* 126 (2004) 11782–11783.
- [34] J.H.K. Yip, J. Wu, K.-Y. Wong, K.P. Ho, C.S.-N. Pun, J.J. Vittal, Electronic Communication Mediated by a PtI–PtI σ -Bond, *Organometallics*. 21 (2002) 5292–5300.
- [35] H. Meerwein, Triethyloxonium Fluoroborate, *Org. Synth.* 46 (1966) 113–115.
- [36] Z. Lamprecht, S.G. Radhakrishnan, A. Hildebrandt, H. Lang, D.C. Liles, N. Weststrate, S. Lotz, D.I. Bezuidenhout, Mono-, di- and tetra-rhenium Fischer carbene complexes with thienothiophene substituents, *Dalton Trans.* 46 (2017) 13983–13993.
- [37] E.O. Fischer, G. Kreis, F.R. Kreissl, W. Kalbfus, E. Winkler, Übergangsmetall-carbin-

komplexe. II. trans-halogeno-diäthylaminocarbin-tetracarbonyl-komplexe des wolframs aus äthoxydiäthylaminocarbenpentacarbonyl-wolfram(0), *J. Organomet. Chem.* 65 (1974) C53–C56.

- [38] M. Krejčík, M. Daněk, F. Hartl, Simple construction of an infrared optically transparent thin-layer electrochemical cell. Applications to the redox reactions of ferrocene, $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}(\text{CO})_3(3,5\text{-di-}t\text{-butyl-catecholate})$ -, *J. Electroanal. Chem.* 317 (1991) 179–187.
- [39] R.W.W. Hooft, Collect Software, Nonius B.V., (1998).
- [40] Z. Otwinowski, W. Minor, Processing of X-ray diffraction data collected in oscillation mode, *Methods Enzymol.* 276 (1997) 307–326.
- [41] SADBS 2.10. Bruker-AXS inc., (2002).
- [42] G.M. Sheldrick, A short history of SHELX, *Acta Crystallogr. Sect. A.* 64 (2008) 112–122.
- [43] G.M. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination, *Acta Crystallogr. Sect. A.* 71 (2015) 3–8.
- [44] A.L. Spek, PLATON SQUEEZE: A tool for the calculation of the disordered solvent contribution to the calculated structure factors, *Acta Crystallogr. Sect. C.* 71 (2015) 9–18.