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Synthesis and Reactivity of an Aminocarbene Osmium Complex Formed by Double C–H Activation of a NCH_3 Unit

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Dedicated to Professor Johann Weis on the occasion of his 65th birthday

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The reaction of $[OsCl_2(PPh_3)_3]$ (**1**) with $iPr_2PCH_2CH_2NMe_2$ in 2-propanol under reflux affords the Fischer-type aminocarbene complex *cis*,*cis*-$[OsCl_2\{\kappa^2(C,P)\text{-}CHN(CH_3)CH_2CH_2P iPr_2\}\{\kappa^2(P,N)\text{-}iPr_2PCH_2CH_2NMe_2\}]$ (**2**) by double C–H activation of one NCH_3 group. While treatment of **2** with phenylacetylene leads to the vinylidene complex *cis*,*trans*-$[OsCl_2(C{=}CHPh)\{\kappa^2(C,P)\text{-}CHN(CH_3)CH_2CH_2PiPr_2\}\{\kappa(P)\text{-}iPr_2PCH_2CH_2NMe_2\}]$ (**3**) by partial opening of the *P*,*N*-chelate bond, the reaction of **2** with CO and CN*t*Bu gives rise to ionic compounds of type $[OsCl(L)\{\kappa^2(C,P)\text{-}CHN(CH_3)CH_2CH_2P iPr_2\}\{\kappa^2(P,N)\text{-}iPr_2PCH_2CH_2OMe\}]Cl$ (**4**: L = CO, **5**: L = CN*t*Bu) by substitution of one chloro ligand.

Introduction

After various attempts in our laboratory and by others[1,2] to prepare coordinatively unsaturated osmium(II) complexes of the general composition $[OsX_2(PR_3)_2]$ (X = halide) as analogues of the well-known iron compounds $[FeX_2(PR_3)_2]$[3] had failed, we recently focussed our interest on the synthesis and reactivity of the corresponding osmium(II) complexes $[OsX_2\{R_2P(CH_2)_nY\}_2]$ with phosphane ethers (n = 2; Y = OMe, OEt) and phosphane esters (n = 1; Y = CO_2Me, CO_2Et) as bidentate, though hemilabile, ligands. These complexes were prepared from the osmium(IV) precursor $[OsH_2Cl_2(PiPr_3)_2]$ and the functionalized phosphane by reductive elimination of H_2 and ligand exchange.[4] The seemingly more simple approach to obtain, for example, $[OsCl_2\{\kappa^2(P,O)\text{-}iPr_2PCH_2CH_2OMe\}_2]$ from $[OsCl_2(PPh_3)_3]$ and $iPr_2PCH_2CH_2OMe$, which in the case of the analogous reaction of $[RuCl_2(PPh_3)_3]$ and $iPr_2PCH_2CH_2OMe$ gave $[RuCl_2\{\kappa^2(P,O)\text{-}iPr_2PCH_2CH_2OMe\}_2]$ in excellent yield,[5] led to a surprising result: instead of the expected product the Fischer-type oxocarbene-osmium(II) complex *cis*,*cis*-$[OsCl_2\{\kappa^2(C,P)\text{-}CHOCH_2CH_2PiPr_2\}\{\kappa^2(P,O)\text{-}iPr_2PCH_2CH_2OMe\}]$ was obtained.[6]

In this paper we report that the phosphaneamine $iPr_2PCH_2CH_2NMe_2$ behaves similar to the phosphane ether $iPr_2PCH_2CH_2OMe$ and affords upon treatment with $[OsCl_2(PPh_3)_3]$ an aminocarbene-osmium(II) derivative. The reactivity of this complex toward some nucleophilic substrates illustrates the inert nature of the carbene–osmium bond.

Results and Discussion

As previously described, the oxocarbene-osmium(II) complex *cis*,*cis*-$[OsCl_2\{\kappa^2(C,P)\text{-}CHOCH_2CH_2PiPr_2\}\{\kappa^2(P,O)\text{-}iPr_2PCH_2CH_2OMe\}]$ could be prepared from either $OsCl_3{\cdot}3H_2O$ or $[OsCl_2(PPh_3)_3]$ (**1**) and $iPr_2PCH_2CH_2OMe$.[6] Since the yield of the product was significantly higher with $OsCl_3{\cdot}3H_2O$ as the precursor, we first treated this compound with $iPr_2PCH_2CH_2NMe_2$. However, the reaction of $OsCl_3{\cdot}3H_2O$ with $iPr_2PCH_2CH_2NMe_2$ in 2-propanol under reflux gave a mixture of products which, based on the spectroscopic data, contained only about 40–50% of the aminocarbene complex **2**. Attempts to separate **2** from the byproducts failed. With the triphenylphosphane-osmium(II) derivative **1** and $iPr_2PCH_2CH_2NMe_2$ as the starting materials and benzene as solvent, the yield of **2**, isolated as a pale yellow air-stable solid, was 71% (Scheme 1). Typical spectroscopic features of **2** are (1) the signal of the =CH carbene proton at δ = 13.14 ppm in the ^1H NMR, (2) the low-field resonance at δ = 220.0 ppm for the Os=C carbon atom in the ^{13}C NMR, and (3) the two doublets at δ = 16.3 and –18.95 ppm in the ^{31}P NMR spectra. The small $^{31}P,^{31}P$ coupling constant of 7.3 Hz is in agreement with a *cis* position of the two phosphorus atoms. We note that the molecular structure of the related oxocarbene complex *cis*,*cis*-$[OsCl_2\{\kappa^2(C,P)\text{-}CHOCH_2CH_2PiPr_2\}\{\kappa^2(P,O)\text{-}iPr_2\text{-}$

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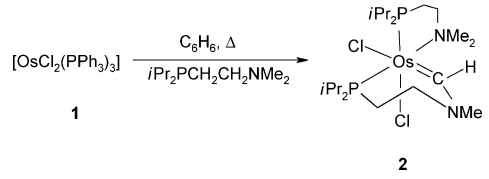
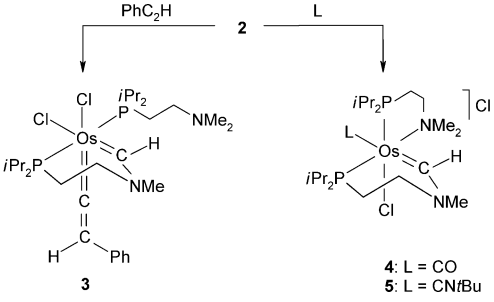
PCH_2CH_2OMe}] was determined crystallographically; the result confirmed that the two P*i*Pr_2 units as well as the two chloro ligands are *cis*-disposed.[6]



Scheme 1.

The reaction of **2** with phenylacetylene gave the vinylidene complex **3** (see Scheme 2) in almost quantitative yield. The compound is possibly formed via the isomeric alkyne- and alkynyl(hydrido) species as intermediates. It represents one of the rare examples, in which a carbene *and* a vinylidene ligand are linked to a single transition metal atom.[7] The ^{1}H NMR spectrum of **3** displays a broadened signal for the = C*H*R proton at δ = 12.18 ppm, a doublet-of-doublets for the vinylidene C=C*H*R proton at δ = 2.30 ppm, and two singlets for the NCH_3 protons at δ = 3.50 and 2.77 ppm in the ratio of 1:2. The appearance of two signals instead of three for the NCH_3 protons indicates that the NMe_2 unit is uncoordinated und that during the formation of **3** a cleavage of the Os–N bond of the *P*,*N*-bonded chelate ring occurred. The ^{13}C NMR spectrum of **3** shows for the vinylidene *C*=CHR and the carbene *C*HR carbon atoms two doublet-of-doublets at δ = 298.9 and δ = 215.5 ppm; the chemical shift of the latter is nearly identical to that of the related oxocarbene complex (δ = 213.0 ppm).[6] The ^{31}P NMR spectrum of **3** displays the typical pattern of an AB spin system with two narrow signals at δ = –0.7 and –2.5 ppm. The large ^{31}P,^{31}P coupling constant of 294.5 Hz supports a *trans* disposition of the two P*i*Pr_2 units.



Scheme 2.

In contrast to phenylacetylene, CO reacted with **2** at room temperature and afforded complex **4** as an air-stable solid in 64% yield. Based on the elemental analysis, at first we assumed that **4** is an analog of the carbene(vinylidene) derivative **3**. However, solutions of **4** in CH_2Cl_2 revealed a molar conductivity Λ 58 $cm^2\,\Omega^{-1}\,mol^{-1}$, which is nearly the same as for corresponding 1:1 electrolytes.[4] Although the relevant NMR spectroscopic data of **4** [δ(C*H*R) = 11.38 ppm; δ(*C*HR) = 231.2 ppm] differ markedly to those of **3** [δ(C*H*R) = 12.18 ppm; δ(*C*HR) = 215.5 ppm], they nevertheless support the presence of a secondary carbene unit. The ^{31}P NMR spectrum of **4** shows two doublets at δ = 23.6 and –6.7 ppm with a ^{31}P,^{31}P coupling constant of 5.3 Hz that, in contrast to **3**, indicates a *cis* disposition of the two phosphorus atoms. In agreement with this proposal are the values of the ^{31}P,^{187}Os coupling constants (259.2 and 226.8 Hz, determined from the satellites in the ^{31}P NMR spectrum), which are significantly different to those of *all-trans*-[$OsCl_2(CO)_2${$\kappa(P)$-*i*$Pr_2PCH_2CH_2OMe$}$_2$] (162.8 Hz) and *cis*,*cis*,*trans*-[$OsCl_2(CO)_2${$\kappa(P)$-*i*$Pr_2PCH_2CH_2OMe$}$_2$] (149.7 Hz).[4] These two complexes contain a linear P–Os–P unit.

The question, which of the possible diastereoisomers of **4** is present in the crystal, was answered by an X-ray diffraction study.[8] The result illustrates that the structure of the cation of **4** is similar to that of the oxocarbene-osmium(II) complex *cis*,*cis*-[$OsCl_2${$\kappa^2(C,P)$-$CHOCH_2CH_2P$*i*Pr_2}{κ^2-(*P*,*O*)-*i*$Pr_2PCH_2CH_2OMe$}]. The difference is that the carbene carbon atom is *trans* disposed to CO and not to the chloro ligand. The Os–$C_{carbene}$ distance [2.123(7) Å] in **4** is elongated compared to the uncharged compound *cis*,*cis*-[$OsCl_2${$\kappa^2(C,P)$-$CHOCH_2CH_2P$*i*Pr_2}{$\kappa^2(P,O)$-*i*$Pr_2PCH_2CH_2OMe$}] [1.83(1) Å],[6] which reflects the *trans* influence of CO on one hand and the positive charge of the cationic complex on the other. Both effects lead to a weakening of the Os–C(carbene) bond. The C–N distance in the chelate ring containing the carbene unit [1.285(8) Å] is significantly shorter than that expected for a C–N single bond and indicates increased π-donation from nitrogen to carbon. Taking into account that the sum of the bond angles around nitrogen amounts to 360°, the aminocarbene complex **4** is thus best described by two major resonance forms (Os–CH=N vs. Os=CH–N) leading to effective Os–C and C–N bond orders between 1 and 2. The Os–Cl bond length [2.465(2) Å] and the P–Os–P bond angle [104.87(6)°] of **4** are nearly identical to that of the oxocarbene-osmium(II) derivative, mentioned above.[6] The entire stereochemistry of **4** resembles that of a distorted octahedron with some angles that are smaller: Cl–Os–$C_{carbene}$ 85.0(2)°, Cl–Os–N 82.9(1)°, P–Os–N 83.2(1)°. Other angles are larger than 90°, P–Os–P in particular: 104.87(6)°.

The reaction of **2** with *tert*-butyl isocyanide in benzene took a similar course to that with CO and afforded the ionic complex **5** as a pale green solid in moderate yield. Characteristic NMR spectroscopic data of **5** are a slightly broadened singlet for the = C*H*R proton at δ = 11.50 ppm, a doublet-of-doublets for the = *C*HR carbene carbon atom at δ = 231.0 ppm, and two doublets for the ^{31}P nuclei at δ = 20.7 and –8.8. The small ^{31}P,^{31}P coupling constant of 5.8 Hz is consistent with a *cis* disposition of the two P*i*Pr_2 groups. Since solutions of **5** in CH_2Cl_2 show a molar conductivity which is almost the same as that of **4**, we assume, that the structure of the two complexes is quite similar.

In conclusion, our work has shown that secondary aminocarbene-osmium complexes, in which the carbene fragment is part of a five-membered chelate ring, can be prepared by double C–H activation of one of the NCH_3 groups of *i*$Pr_2PCH_2CH_2NMe_2$. We assume that in the initial step of the reaction of the **1** with *i*$Pr_2PCH_2CH_2NMe_2$ the phos-

phaneamine displaces the PPh_3 ligands of **1** and generates the bis(chelate) complex $[OsCl_2\{\kappa^2(P,N)\text{-}iPr_2PCH_2CH_2NMe_2\}_2]$ as intermediate. In the next step, probably insertion of the metal into one of the C–H bonds of the NCH_3 unit occurs, leading to a labile hydridoosmium(II) species with an $OsH\{CH_2N(CH_3)R\}$ core. The following elimination of H_2 would afford the osmium carbene. With regard to this mechanism, we note that recently Carmona[9] and Grubbs[10] reported that the reactions of a bis(ethene) iridium(I) and a dihydrido iridium(III) complex with methyl ethers CH_3OR (R = CMe_3, $CH_2CH_2CH_2CH_3$, CH_2CH_2OMe) produced Fischer-type iridium oxocarbenes in excellent yields. The authors proposed that the decisive step of these processes consists in the elimination of, respectively, C_2H_4 and H_2 from the starting material and the formation of a coordinatively unsaturated iridium(I) intermediate to which the ether coordinates. Since methylamines such as TMEDA behave analogously,[11,12] it is to expect that in the time to come the activation of two α-C–H bonds of an ether or amine functionality could supplement the well-known synthetic routes to Fischer-type transition metal carbenes.[13]

Experimental Section

General: All reactions were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**[14] and the phosphaneamine[15] were prepared as described in the literature. NMR spectra were recorded on Bruker AC 200 and Bruker AMX 400 instruments at room temperature, if not otherwise stated. IR spectra were recorded on a Perkin–Elmer 1420 infrared spectrometer. Melting points were measured by DTA.

1. Preparation of *cis*,*cis*-[$OsCl_2\{\kappa^2(C,P)$-$CHN(CH_3)CH_2CH_2P$*i*$Pr_2\}\{\kappa^2(P,N)$-*i*$Pr_2PCH_2CH_2NMe_2\}$] (2): A solution of **1** (214 mg, 0.37 mmol) in benzene (10 mL) was treated with *i*$Pr_2PCH_2CH_2NMe_2$ (234 μL, 1.10 mmol) and stirred for 3 days under reflux. After the solution was cooled to room temperature, the solvent was evaporated in vacuo. The oily residue was layered with hexane (10 mL) and the suspension was stirred for 6 h at room temperature. A pale yellow solid precipitated, which was filtered, washed for three times with 2-mL portions of pentane and dried; yield 166 mg (71%); m.p. 176 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.14 (d, $^3J_{P,H}$ = 4.2 Hz, 1 H, Os=CH), 4.42, 3.35, 3.27 (all m, 1 H each, PC*H*CH_3 or PCH_2 or NCH_2), 3.23 (s, 3 H, NCH_3), 2.95, 2.84 (both m, 1 H each, PC*H*CH_3 or PCH_2 or NCH_2), 2.80, 2.40 (both s, 3 H each, NCH_3), 2.30, 1.69 (both m, 1 H each, PCH_2 or NCH_2 or PC*H*CH_3), 1.91 (m, 3 H, PCH_2 or NCH_2 or PC*H*CH_3), 1.66 (dd, $^3J_{P,H}$ = 13.8, ^3J(H,H) = 7.2 Hz, 3 H, PCHC*H*$_3$), 1.46 (m, 2 H, PCH_2 or NCH_2 or PC*H*CH_3), 1.37 (dd, $^3J_{P,H}$ = 14.2, $^3J_{H,H}$ = 7.3 Hz, 3 H, PCHC*H*$_3$), 1.29 (dd, $^3J_{P,H}$ = 11.5, $^3J_{H,H}$ = 7.3 Hz, 3 H, PCHC*H*$_3$), 1.19 (dd, $^3J_{P,H}$ = 12.3, $^3J_{H,H}$ = 7.2 Hz, 3 H, PCHC*H*$_3$), 1.13 (dd, $^3J_{P,H}$ = 16.3, $^3J_{H,H}$ = 7.2 Hz, 3 H, PCHC*H*$_3$), 1.10 (dd, $^3J_{P,H}$ = 15.8, $^3J_{H,H}$ = 7.2 Hz, 3 H, PCHC*H*$_3$), 1.04 (dd, $^3J_{P,H}$ = 12.7, $^3J_{H,H}$ = 7.1 Hz, 3 H, PCHC*H*$_3$), 0.97 (dd, $^3J_{P,H}$ = 13.2, $^3J_{H,H}$ = 7.2 Hz, 3 H, PCHC*H*$_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 220.0 (dd, $^2J_{P,C}$ = 7.6 Hz, Os=C), 61.6 (s, NCH_2), 50.6, 49.7 (both s, NCH_3), 49.7 (s, NCH_2), 38.4 (d, $^1J_{P,C}$ = 28.4 Hz, P*C*HCH$_3$), 27.1 (d, $^1J_{P,C}$ = 28.4 Hz, P*C*HCH$_3$), 26.4 (d, $^1J_{P,C}$ = 26.6 Hz, P*C*HCH$_3$), 24.5 (d, $^1J_{P,C}$ = 26.6 Hz, PCH_2), 23.3 (d, $^1J_{P,C}$ = 23.6 Hz, P*C*HCH$_3$), 21.7 (d, $^1J_{P,C}$ = 31.8 Hz, PCH_2), 21.0 (d, $^2J_{P,C}$ = 6.0 Hz, PCH*C*H$_3$), 20.5 (d, $^2J_{P,C}$ = 7.0 Hz, PCH*C*H$_3$), 20.4 (d, $^2J_{P,C}$ = 4.7 Hz, PCH*C*H$_3$), 21.1, 19.8, 19.7, 19.6, 19.2 (all s, PCH*C*H$_3$) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 16.3 (d, $^2J_{P,P}$ = 7.3, $^1J_{Os,P}$ = 288.5 Hz), –18.95 (d, $^2J_{P,P}$ = 7.3, $^1J_{Os,P}$ = 282.0 Hz) ppm. $C_{20}H_{46}Cl_2N_2OsP_2$ (637.7): calcd. C 37.67, H 4.39, N 7.27; found C 37.24, H 3.97, N 6.98.

2. Preparation of *cis*,*trans*-[$OsCl_2$(C=CHPh)$\{\kappa^2(C,P)$-$CHN(CH_3)CH_2CH_2P$*i*$Pr_2\}\{\kappa(P)$-*i*$Pr_2PCH_2CH_2NMe_2\}$] (3): A solution of **2** (82 mg, 0.13 mmol) in a mixture of benzene (10 mL) and dichloromethane (5 mL) was treated with phenylacetylene (500 μL, 4.55 mmol) and stirred for 2 days under reflux. After the solution was cooled to room temperature, the solvent was evaporated in vacuo. The oily residue was layered with diethyl ether (10 mL) and the suspension stored for 3 h. An orange-brown solid separated which was filtered, washed twice with pentane (3 mL each) and dried; yield 82 mg (86%); m.p. 163 °C (dec.). IR (C_6H_6): $\tilde{\nu}$ = 1575 [ν(C=C)] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.18 (br. s, 1 H, Os=CH), 7.14 (m, 2 H, C_6H_5), 6.80 (m, 1 H, C_6H_5), 6.73 (m, 2 H, C_6H_5), 4.48, 4.03, 3.71, 3.59 (all m, 1 H each, PC*H*CH_3 or PCH_2 or NCH_2), 3.50 (s, 3 H, NCH_3), 2.84 (m, 3 H, PC*H*CH_3 or PCH_2 or NCH_2), 2.77 (s, 6 H, NCH_3), 2.49, 2.40 (both m, 2 H each, PC*H*CH_3 or PCH_2 or NCH_2), 2.30 (dd, $^3J_{P,H}$ = $^3J_{P',H}$ = 3.3 Hz, 1 H, Os=C=C*H*Ph), 1.86 (m, 1 H, PC*H*CH_3 or PCH_2 or NCH_2), 1.35 (br. dd, $^3J_{P,H}$ = 14.9, $^3J_{H,H}$ = 7.1 Hz, 3 H, PCHC*H*$_3$), 1.30 (br. d, $^3J_{H,H}$ = 7.1 Hz, 3 H, PCHC*H*$_3$), 1.26 (br. d, $^3J_{H,H}$ = 7.1 Hz, 6 H, PCHC*H*$_3$), 1.22 (br. d, $^3J_{H,H}$ = 7.0 Hz, 3 H, PCHC*H*$_3$), 1.19 (br. d, $^3J_{H,H}$ = 6.9 Hz, 3 H, PCHC*H*$_3$), 1.07 (br. d, $^3J_{H,H}$ = 7.0 Hz, 3 H, PCHC*H*$_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 298.9 (dd, $^2J_{P,C}$ = $^2J_{P',C}$ = 11.8 Hz, Os=*C*=CHPh), 215.5 (dd, $^2J_{P,C}$ = $^2J_{P',C}$ = 9.4 Hz, Os=CH), 129.2 (s, *ipso*-C of C_6H_5), 129.0, 128.9, 125.9 (all s, C_6H_5), 112.0 (s, Os=C=*C*HPh), 66.5 (s, NCH_3), 55.6, 54.4 (both s, NCH_2), 53.2 (s, NCH_3), 27.2 (dd, $^1J_{P,C}$ = 22.3, $^3J_{P',C}$ = 7.0 Hz, P*C*HCH$_3$), 25.3 (dd, $^1J_{P,C}$ = 20.0, $^3J_{P',C}$ = 4.1 Hz, P*C*HCH$_3$), 24.7 (dd, $^1J_{P,C}$ = 21.1, $^3J_{P',C}$ = 4.7 Hz, P*C*HCH$_3$), 20.1, 20.0, 19.7 (all s, PCH*C*H$_3$), 18.9 (d, $^3J_{P',C}$ = 4.7 Hz, P*C*HCH$_3$), 18.6, 18.5, 18.4, 18.2 (all s, PCH*C*H$_3$), 14.5 (br. d, $^1J_{P,C}$ = 22.2 Hz, PCH_2), 12.8 (br. d, $^1J_{P,C}$ = 24.6 Hz, PCH_2) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): AB spin system, δ_A = –0.7, δ_B = –2.5 ($^2J_{A,B}$ = 294.5 Hz) ppm. $C_{28}H_{52}Cl_2N_2OsP_2$ (739.8): calcd. C 45.46, H 7.08, N 3.79; found C 45.28, H 7.07, N 3.17.

3. Preparation of [$OsCl(CO)\{\kappa^2(C,P)$-$CHN(CH_3)CH_2CH_2P$*i*$Pr_2\}\{\kappa^2(P,N)$-*i*$Pr_2PCH_2CH_2NMe_2\}$]Cl (4): A slow stream of CO was passed through solution of **2** (48 mg, 0.08 mmol) in methanol (5 mL) for 5 min. After the solvent was evaporated in vacuo, the oily residue was layered with pentane (10 mL) and the suspension stirred for 2 h. A pale yellow solid separated which was filtered, washed twice with pentane (3 mL each) and dried; yield 32 mg (64%); m.p. 118 °C (dec.); molar conductivity Λ 58 cm$^2\Omega^{-1}$mol^{-1}. IR (C_6H_6): $\tilde{\nu}$ = 1915 [ν(CO)] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.38 (s, 1 H, Os=CH), 4.65 (m, 1 H, PC*H*CH_3 or PCH_2 or NCH_2), 4.01 (s, 3 H, NCH_3), 3.65 (m, 1 H, PC*H*CH_3 or PCH_2 or NCH_2), 3.44 (m, 3 H, PC*H*CH_3 or PCH_2 or NCH_2), 3.09 (s, 3 H, NCH_3), 2.95 (m, 1 H, PC*H*CH_3 or PCH_2 or NCH_2), 2.81 (s, 3 H, NCH_3), 2.75, 2.64, 2.54, 2.38, 2.08, 1.78 (all m, 1 H each, PCH_2 or NCH_2 or PC*H*CH_3), 1.51 (dd, $^3J_{P,H}$ = 13.2, $^3J_{H,H}$ = 7.2 Hz, 3 H, PCHC*H*$_3$), 1.28 (br. d, $^3J_{H,H}$ = 7.0 Hz, 3 H, PCHC*H*$_3$), 1.23 (m, 12 H, PCHC*H*$_3$), 1.12 (dd, $^3J_{P,H}$ = 15.4, $^3J_{H,H}$ = 7.1 Hz, 3 H, PCHC*H*$_3$) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 231.2 (br. s, Os=C), 192.3 (dd, $^2J_{P,C}$ = $^2J_{P',C}$ = 8.3 Hz, OsCO), 64.9 (s, NCH_2), 58.6, 56.1 (both s, NCH_3), 52.1 (s, NCH_2), 51.6 (s, NCH_3), 38.2 (d, $^1J_{P,C}$ = 33.0 Hz, P*C*HCH$_3$), 28.9 (d, $^1J_{P,C}$ = 29.2 Hz, P*C*HCH$_3$), 28.7 (d, $^1J_{P,C}$ = 29.2 Hz, P*C*HCH$_3$), 27.3 (d, $^1J_{P,C}$ = 30.5 Hz, P*C*HCH$_3$), 26.2, 22.1 (both d, $^1J_{P,C}$ = 30.5 Hz, PCH_2), 21.3, 20.5,

20.2, 20.1, 19.9, 19.8, 19.6, 19.1 (all s, PCH*C*H$_3$) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 23.6 (d, $^2J_{P,P}$ = 5.3, $^1J_{Os,P}$ = 259.2 Hz), –6.7 (d, $^2J_{P,P}$ = 5.3, $^1J_{Os,P}$ = 226.8 Hz) ppm. $C_{21}H_{46}Cl_2N_2OOsP_2$ (665.4): calcd. C 37.91, H 6.93, N 4.21; found C 37.53, H 6.61, N 3.97.

4. Preparation of [OsCl(CN*t*Bu){κ^2(*C*,*P*)-CHN(CH$_3$)CH$_2$CH$_2$-P*i*Pr$_2$}{κ^2(*P*,*N*)-*i*Pr$_2$PCH$_2$CH$_2$NMe$_2$}]Cl (5): A solution of **2** (55 mg, 0.09 mmol) in benzene (10 mL) was treated with CN*t*Bu (200 μL, 1.77 mmol) and stirred for 30 min at room temperature. After the solvent was evaporated in vacuo, the oily residue was layered with pentane (10 mL) and the suspension stirred for 2 h. A pale green solid separated which was filtered, washed twice with pentane (3 mL each) and dried; yield 22 mg (35%); molar conductivity Λ 48 cm$^2\Omega^{-1}$mol^{-1}. IR (C_6H_6): $\tilde{\nu}$ = 2090 [ν(CN)] cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 11.50 (s, 1 H, Os=CH), 4.34 (m, 1 H, PC*H*CH$_3$ or PCH$_2$ or NCH$_2$), 3.71 (s, 3 H, NCH$_3$), 3.45 (m, 1 H, PC*H*CH$_3$ or PCH$_2$ or NCH$_2$), 3.15 (m, 3 H, PC*H*CH$_3$ or PCH$_2$ or NCH$_2$), 2.81 (s, 3 H, NCH$_3$), 2.65 (m, 1 H, PC*H*CH$_3$ or PCH$_2$ or NCH$_2$), 2.60 (s, 3 H, NCH$_3$), 2.48–2.15 (br. m, 4 H, PC*H*CH$_3$ or PCH$_2$ or NCH$_2$), 1.88, 1.57 (both m, 1 H each, PC*H*CH$_3$ or PCH$_2$ or NCH$_2$), 1.34 (s, 9 H, CNC(CH$_3$)$_3$), 1.44–0.90 (br. m, 24 H, PCHC*H*$_3$) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 231.0 (dd, $^2J_{P,C}$ = $^2J_{P',C}$ = 3.4 Hz, Os=C), 145.8 (br. s, Os*C*N*t*Bu), 63.8 (s, NCH$_2$), 56.9, 56.0 (both s, NCH$_3$), 56.4 (s, CN*C*(CH$_3$)$_3$), 51.3 (s, NCH$_2$), 51.0 (s, NCH$_3$), 38.4 (d, $^1J_{P,C}$ = 31.7 Hz, P*C*HCH$_3$), 30.7 (s, CNC(*C*H$_3$)$_3$), 29.2 (d, $^1J_{P,C}$ = 30.0 Hz, P*C*HCH$_3$), 28.2 (d, $^1J_{P,C}$ = 28.0 Hz, P*C*HCH$_3$), 26.8 (d, $^1J_{P,C}$ = 29.2 Hz, P*C*HCH$_3$), 25.4 (d, $^1J_{P,C}$ = 29.3 Hz, PCH$_2$), 22.0 (d, $^1J_{P,C}$ = 30.6 Hz, PCH$_2$), 21.3, 20.5, 20.1, 19.5, 19.2, 18.8 (all s, PCH*C*H$_3$) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 20.7, –8.8 (both d, $^2J_{P,P}$ = 5.8 Hz) ppm. $C_{25}H_{55}Cl_2N_3OsP_2$ (720.8): calcd. C 41.66, H 7.69, N 5.83; found C 41.98, H 8.01, N 5.60.

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