Conformational Isomers of Bis(*tert*-butylphosphine)osmium Complexes

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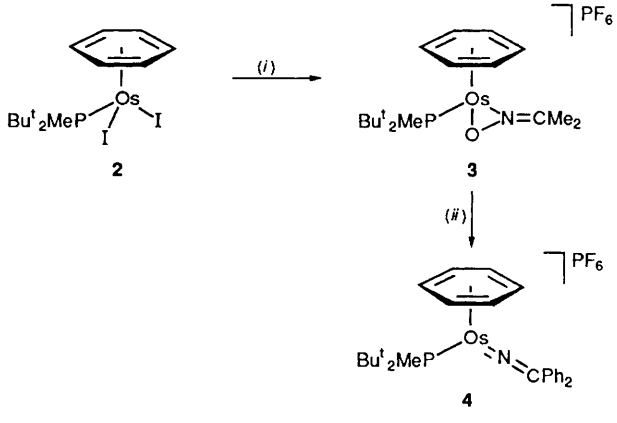
Reaction of $[OsI_2(C_6H_6)(PMeBu^t_2)]$ with $Na[ON{=}CMe_2]$ in methanol, in presence of KPF_6, afforded the oximato compound $[Os(C_6H_6)(\eta^2\text{-}ON{=}CMe_2)(PMeBu^t_2)]PF_6$ which on further reaction with $HN{=}CPh_2$ gave the azavinylidene complex $[Os(C_6H_6)(=N{=}CPh_2)(PMeBu^t_2)]PF_6$. By using a similar synthetic route, the bis(*tert*-butylphosphine)osmium(II) derivatives $[OsX_2(arene)(PHBu^t_2)]$, $[Os(arene)(\eta^2\text{-}ON{=}CMe_2)(PHBu^t_2)]PF_6$ and $[Os(arene)(=N{=}CPh_2)(PHBu^t_2)]PF_6$ (arene = C_6H_6 or $C_6H_3Me_3$-1,3,5; X = Cl or I) were obtained, in most cases almost quantitatively. The NMR spectra of all the latter complexes and of $[Os(C_6H_6)(\eta^2\text{-}ON{=}CMe_2)(PMeBu^t_2)]PF_6$ are temperature-dependent and thus indicative of a dynamic behaviour in solution. The most reasonable explanation for these observations is that due to a hindered rotation around the Os–P axis conformational isomers are formed. The energy barrier for the conversion significantly depends on the type of the non-phosphine ligands co-ordinated to osmium and is, for arene = C_6H_6, in $[Os(arene)(=N{=}CPh_2)(PHBu^t_2)]PF_6$ higher than in $[OsX_2(arene)(PHBu^t_2)]$ and in the mesitylene complexes higher than in the benzene derivatives. For $[Os(C_6H_6)(=N{=}CPh_2)(PHBu^t_2)]PF_6$, a value of $\Delta G^{\ddagger}$ for the rotational barrier of *ca.* 60 kJ mol^{-1} has been calculated.

Following our work on vinylidene osmium complexes $[Os(C_6H_6)(=C{=}CHR)(PR'_3)]$ (R = alkyl or aryl, PR'_3 = PPr^i_3 or $PMeBu^t_2$),[1] we recently reported that the corresponding azavinylidene[2] derivatives $[Os(C_6H_6)(=N{=}CRR')(PMeBu^t_2)]PF_6$ (R = H, Me or Ph; R' = Me or Ph) may be prepared in good yields by reaction of the hydrido compound $[OsH(I)(C_6H_6)(PMeBu^t_2)]$ with $AgPF_6$ and ketoximes.[3] In two cases the cationic complexes $[OsH(C_6H_6)\{N(OH){=}CRR'\}(PMeBu^t_2)]PF_6$ have been characterized by IR and NMR spectroscopy as intermediates which react by elimination of water to give the final products.

When we tried to prepare analogous azavinylidene metal compounds with phosphine ligands other than $PMeBu^t_2$ we found that an alternative route to complexes of the general type $[M(arene)(=N{=}CRR')L]PF_6$ (M = Ru or Os, L = tertiary phosphine) is feasible. It starts with the dichloro or diiodo metal derivatives $[MX_2(arene)L]$ which are first converted with $Na[ON{=}CRR']$ into the cationic oximato compounds $[M(arene)(\eta^2\text{-}ON{=}CRR')L]^+$. On treatment with imines (in particular $HN{=}CPh_2$), they undergo a ligand exchange which leads to the azavinylidene ruthenium or osmium complexes.[4,5] In the course of this work we observed that the cationic species $[Os(arene)(\eta^2\text{-}ON{=}CR'_2)(PRBu^t_2)]^+$ and $[Os(arene)(=N{=}CPh_2)(PRBu^t_2)]^+$ (R = H or Me) show temperature-dependent ^1H and ^{31}P NMR spectra probably due to the formation of rotational isomers. The present paper describes our results in this area.

Results and Discussion

Osmium Complexes with $PMeBu^t_2$ *as Ligand.*—Under conditions similar to those used for the preparation of $[Ru(C_6H_6)(\eta^2\text{-}ON{=}CRR')(PPr^i_3)]PF_6$,[5] the diiodoosmium(II) derivative **2** (see Scheme 1) reacts with $Na[ON{=}CMe_2]$ in methanol, in the presence of KPF_6, to give the yellow oximato complex **3** in 88% yield. On further reaction of **3** with $HN{=}CPh_2$ in dichloromethane the oxime is eliminated and the azavinylidene compound **4** is formed almost quantitatively. It has been identified by comparison of the NMR spectroscopic data with those of an authentic sample.[3]



Scheme 1 (*i*) $Na[ON{=}CMe_2]$, KPF_6; (*ii*) $HN{=}CPh_2$

In the course of the ^{31}P NMR measurements undertaken to confirm the structure proposed for compound **3**, we observed that the signal of the $PMeBu^t_2$ phosphorus is unusually broad. In contrast, the spectrum at −65 °C (in CD_2Cl_2) shows two sharp singlets which differ significantly in their intensities. On warming the solution the two signals broaden and finally coalesce at *ca.* −13 °C (Fig. 1). Above room temperature (in CD_3NO_2) one relatively sharp singlet emerges which has a chemical shift at slightly higher field compared to that found at 25 °C.

The changes observed in the $^1H\text{-}\{^{31}P\}$ NMR spectrum of compound **3** at various temperatures (see Fig. 2) are also indicative of a dynamic behaviour of the cation in solution. Whereas at −65 °C (in CD_2Cl_2) the PCH_3 protons give rise to a sharp singlet at δ 0.83, this signal broadens on raising the temperature and at *ca.* −23 °C completely disappears. At 25 °C, both in CD_2Cl_2 and CD_3NO_2, the PCH_3 resonance is found (slightly broadened) at somewhat lower field (δ 0.8–1.0) and sharpens up again above +50 °C. It is important to note that for the analogous oximato complexes $[M(arene)(\eta^2\text{-}ON{=}CRR')L]PF_6$ (M = Ru or Os, L = PMe_3 or PPr^i_3) a similar

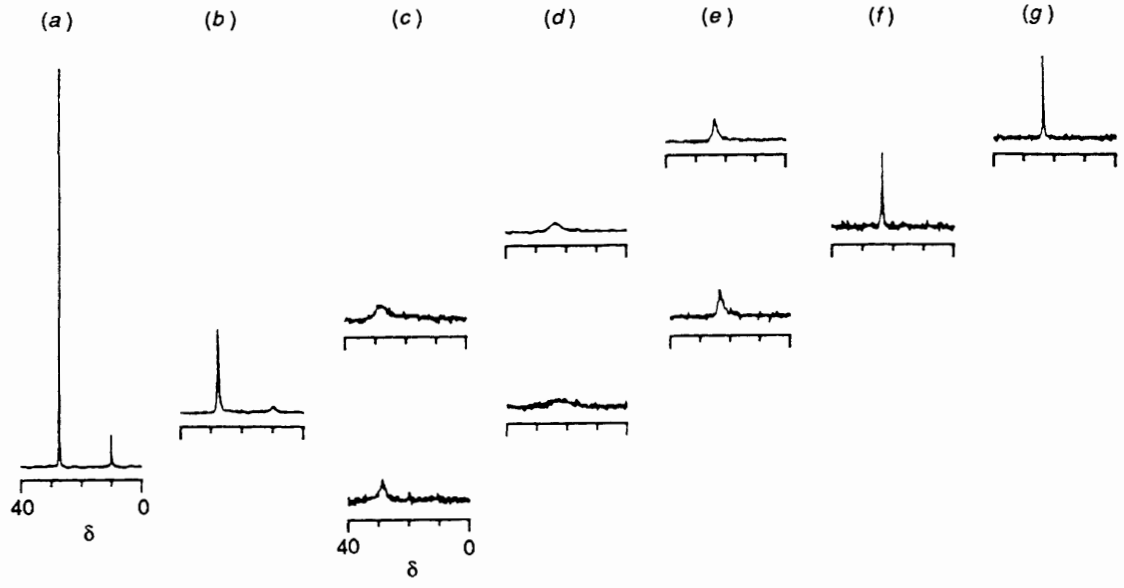


Fig. 1 The ^{31}P NMR spectra (36.2 MHz) of compound **3** at (*a*) 208, (*b*) 228, (*c*) 248, (*d*) 268, (*e*) 298, (*f*) 318 and (*g*) 338 K. Top series: in CD_2Cl_2; bottom series: in CD_3NO_2

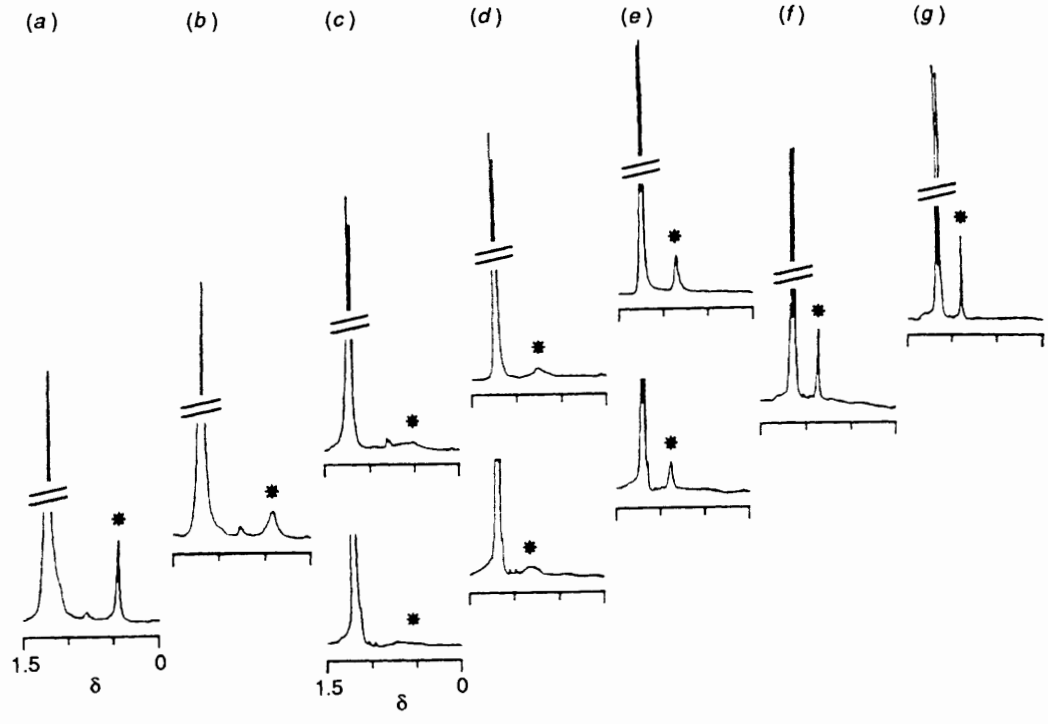


Fig. 2 The ^1H-$\{^{31}P\}$ NMR spectra (90 MHz) of compound **3** in the region δ 1.5–0 at various temperatures (see Fig. 1) [signals of the $PCCH_3$ and PCH_3 (*) protons]. Top series: in CD_2Cl_2; bottom series: in CD_3NO_2

phenomenon has not been observed.[3b,5] As the temperature-dependent changes are most obvious for the $PMeBu^t_2$ phosphorus and PCH_3 signals, we assume that they originate from a hindered rotation around the Os–P bond. Similar observations have recently been made by Bennett *et al.*[6] who found a dynamic behaviour in solution for the ruthenium complex $[Ru(O_2CCF_3)(C_6H_4Me_2\text{-}1,2(PMePh_2)_2]PF_6$.

Complexes with $PHBu^t_2$ *as Ligand.*—In order to gain more insight into the dynamics of sterically crowded metal compounds with phosphine ligands of the general type $PRBu^t_2$, we decided to prepare a series of osmium complexes containing [(Os(arene)$(PHBu^t_2)$)] [arene = C_6H_6 or $C_6H_3Me_3$-1,3,5 (mes)] as a molecular unit. The fact that bis(*tert*-butyl)-phosphine is a useful tool for the detection of rotational isomers has already been demonstrated by Shaw and co-workers[7] in the case of the four- and six-co-ordinated compounds $[MCl_2(PHBu^t_2)_2]$ (M = Pd or Pt), $[MCl(CO)(PHBu^t_2)_2]$ (M = Rh or Ir) and $[RuCl_2(CO)_2(PHBu^t_2)_2]$, respectively.

The preparative route to obtain the benzene and mesitylene osmium complexes with $PHBu^t_2$ as ligand is outlined in Scheme 2. The diiodo and dichloro derivatives **5** and **7** are obtained by conventional means and are transformed into the oximato compounds **8** and **9** upon treatment with $Na[ON{=}CMe_2]$ and KPF_6. The yield is 80–95%. Compounds **8** and **9** react with $HN{=}CPh_2$ in CH_2Cl_2 to give the azavinylidene complexes **10** and **11** nearly quantitatively.

Similar to those of compounds **8**–**11**, the NMR spectra of **5** and **7** are temperature-dependent. At 25 °C in CD_2Cl_2 the $PHBu^t_2$ signal in the ^{31}P NMR spectrum as well as the P*H*Bu^t_2 resonance in the ^1H NMR spectrum is rather broad which possibly reflects a slightly hindered rotation around the Os–P

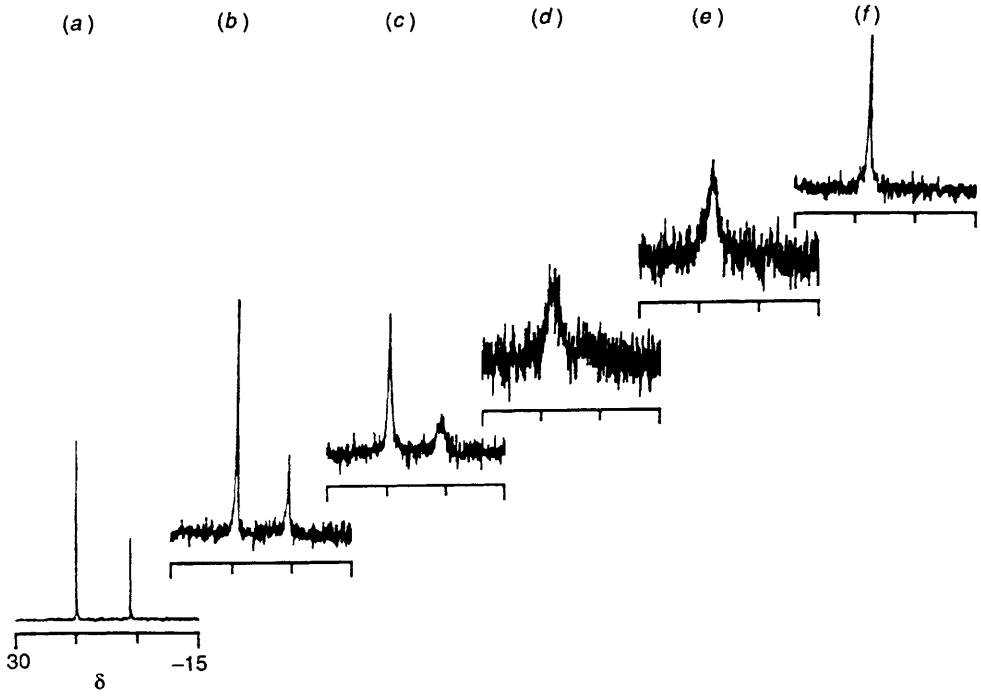
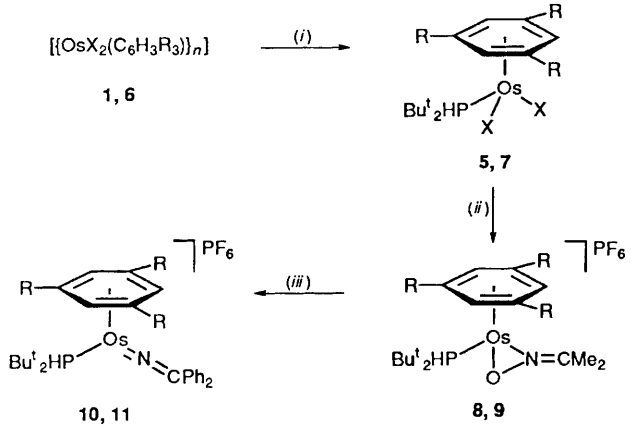


Fig. 3 The ^{31}P NMR spectra (36.2 MHz) of compound **5** in CD_2Cl_2 at (*a*) 193, (*b*) 218, (*c*) 233, (*d*) 253, (*e*) 273 and (*f*) 298 K



Scheme 2 R = H (**1**, **5**, **8**, **10**) or Me (**6**, **7**, **9**, **11**), X = I (**1**, **5**) or Cl (**6**, **7**). (*i*) $PHBu^t_2$; (*ii*) KPF_6, $Na[ON{=}CMe_2]$; (*iii*) $HN{=}CPh_2$

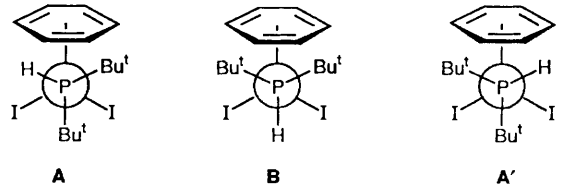


Fig. 4 Rotamers of compound **5** with a staggered conformation along the Os–P axis

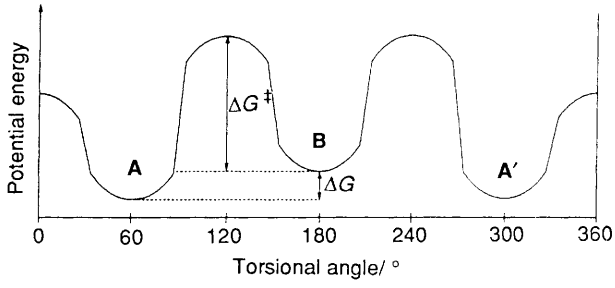


Fig. 5 Schematic energy diagram for the rotamers of compounds **5** and **7**

axis. Whereas on lowering the temperature the phosphorus signal in the ^{31}P NMR spectrum of **7** sharpens, the corresponding resonance of **5** first broadens and then coalesces at *ca.* −10 °C (see Fig. 3). Below −30 °C two singlet resonances appear which at −80 °C sharpen up showing an intensity ratio of *ca.* 2:1. Assuming that for a molecule such as **5** only rotamers with a staggered conformation along the Os–P axis are thermodynamically stable, the species observed at low temperatures in its ^{31}P NMR spectrum probably correspond to **A** (or **A'**) and **B** (see Fig. 4), respectively.

The question of whether the more stable rotamer of compound **5** has the confirmation **A** or **B** is not easy to answer. Although the X-ray structural analyses of the two $PMeBu^t_2$ complexes $[Os(C_6H_6)\{OC(=O)CHMeNH_2\}(PMeBu^t_2)]I$[8] and $[Os(C_6H_6)\{=C(CH_2)_3O\}(PMeBu^t_2)]PF_6$[9] indicate that at least in the crystal lattice the rotamer which has the bulky *tert*-butyl groups relatively close to the arene ring (analogous to **B**) might be preferred, the ^1H NMR spectra of **5** at various temperatures leave no doubt that the energy difference between **A** and **B** is relatively small. Due to the intensity ratio (2:1) of the two signals in the ^{31}P NMR spectrum of **5**, we assume that the signal at δ 16.65 should be assigned to the energetically equivalent rotamers **A** and **A'** while the signal at δ −0.96 corresponds to **B**. In agreement with this the ^1H NMR spectrum shows at −70 °C also two signals for the C_6H_6 and $PCCH_3$ protons which is equally consistent with the presence of two species. The fact that for **A** and **A'** only one doublet for the protons of the two differently oriented *tert*-butyl groups is observed could be due either to the practically identical chemical shift of the expected two signals or, more probably, to a rapid conversion of **A** into **A'** (and *vice versa*) not *via* **B** (see Fig. 5) but by way of a windscreen-wiper motion *via* a transition state in which the Os–C_6H_6(centre) and P–H axis are eclipsed. The latter process is expected to have a considerably lower activation energy than that for the conversion of **A** (or **A'**) into **B** and, therefore, might not be frozen out even at −70 °C. In the low-temperature ^{31}P NMR spectrum of the mesitylene complex **7** only one resonance at δ 18.28 is observed and, therefore, we conclude that its major rotamer has a conformation related to **A** or **A'**, respectively. The other rotamer (corresponding to **B**) should definitely be less stable because of the strong steric hindrance between the aromatic ring and the two neighbouring *tert*-butyl groups.

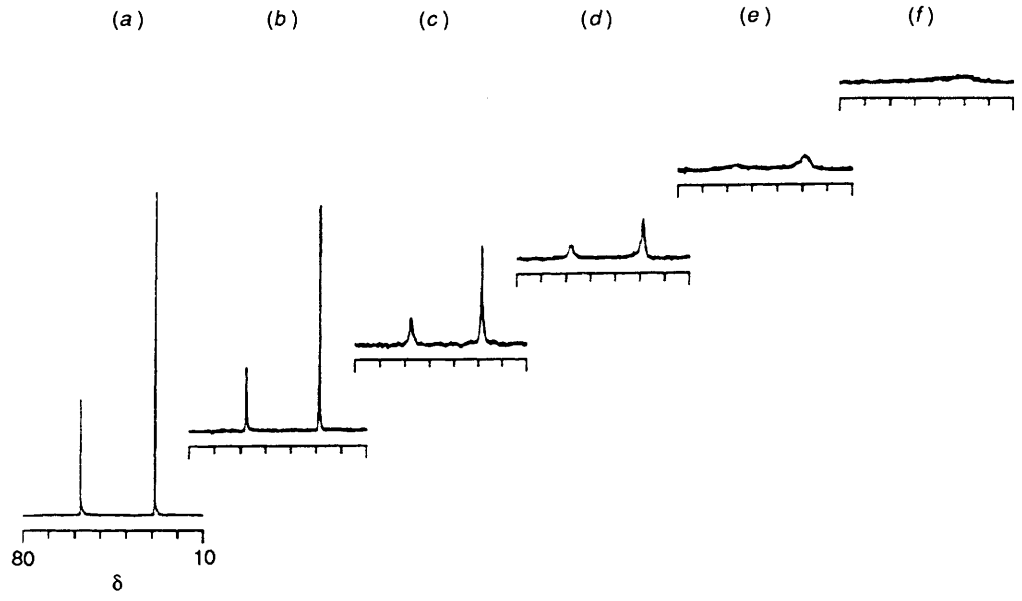


Fig. 6 The ^{31}P NMR spectra (36.2 MHz) of compound **10** in CD_3NO_2 at (*a*) 248, (*b*) 273, (*c*) 298, (*d*) 308, (*e*) 328 and (*f*) 348 K

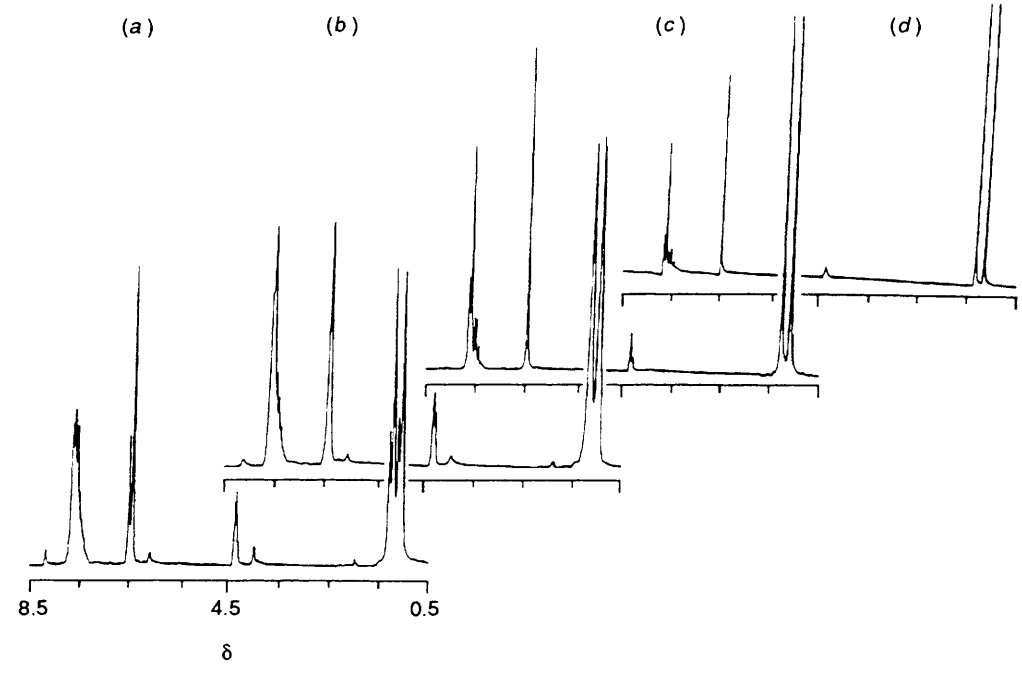


Fig. 7 Proton NMR spectra (90 MHz) of compound **10** in CD_3NO_2 at (*a*) 248, (*b*) 273, (*c*) 298 and (*d*) 348 K

The azavinylidene complexes **10** and **11** show a dynamic behaviour similar to that found for **5** and **7**. Whereas the ^{31}P NMR spectrum of the mesitylene compound **11** displays only one sharp singlet at 25 °C which does not broaden at elevated temperatures, in the room-temperature spectrum of **10** two broad signals appear. They coalesce only at *ca.* +75 °C (see Fig. 6) which indicates that the barrier for rotation around the Os–P axis in **10** is higher than that in **5**.

The presence of two rotamers in solutions of compound **10** in CD_3NO_2 is also obvious from ^1H and ^{13}C NMR measurements. The ratio between the major and the minor component in the ^1H NMR spectrum at −25 °C is *ca.* 2:1 (see Fig. 7), similar to the value observed for **5** at −70 °C. The difference in the chemical shift for the PH signal of the two rotamers is relatively large (*ca.* 2 ppm), and this could be explained by the different shielding of the phosphine proton either by the benzene ligand or the two phenyl substituents of the azavinylidene unit. Since we assume that, of the six possible rotamers (Fig. 8), **A** and **A'** are energetically least favoured and **C** and **C'** lie between **B** and **D**, the conclusion is that the two species observed in the NMR spectra of **10** correspond to the two isomers **B** and **D**. With regard to crystal structural data, it is again worth mentioning that both in $[Os(C_6H_6)(=N=CPh_2)(PMeBu^t_2)]PF_6$[3] and $[Ir(C_5Me_5)(=N=CPh_2)(PMeBu^t_2)]BF_4$[10] the rotamer related to **B** is fixed in the lattice.

In contrast to compounds **5**, **7** and **10**, **11** where a reasonable structural assignment for the two different rotamers is possible, it is much more difficult to predict which of the conformations of the oximato complexes **8** and **9** could be more stable. The temperature dependence of the ^1H and ^{31}P NMR spectra of **8** (see Figs. 9 and 10) clearly indicates that as in the case of **10** (see Figs. 6 and 7) two species in approximately equal quantity are

present at 25 °C and below. The ^{31}P NMR spectrum of the corresponding mesitylene complex **9** displays at room temperature two sharp signals of different intensities indicating that one of the possible rotamers dominates. As no structural data for half-sandwich type ruthenium and osmium compounds with $PHBu^t_2$ or $PRBu^t_2$ and $ON{=}CR'_2{}^-$ as ligands are available, one can only speculate that for **8** and **9** a rotamer related to **A** or **A'** (see Fig. 5) with the oximate anion replacing the two iodo ligands might be energetically preferred.

In order to gain at least a semiquantitative measure of the rotational barrier around the Os–P bond in the azavinylidene complex **10**, the free enthalpy of activation has been determined.[11] Whereas from the ^{31}P NMR spectra (T_c = 348 K), a $\Delta G^{\ddagger}$ of 63.2 kJ mol^{-1} can be calculated, a value of 58 kJ mol^{-1} is obtained from the coalescence of the C_6H_6 and $PCCH_3$ resonances in the ^1H NMR spectra (T_c = 263 K). Although we are not aware of comparable data for the rotational barrier of $M–PHBu^t_2$ or $M–PRBu^t_2$ compounds in the literature, we assume that conformational isomers can probably be detected also for other transition-metal complexes containing those phosphines (in general: PRR'_2 where R' is a sterically demanding substituent) provided that the coordination sphere of the metal causes some steric hindrance for rotation around the M–P bond.

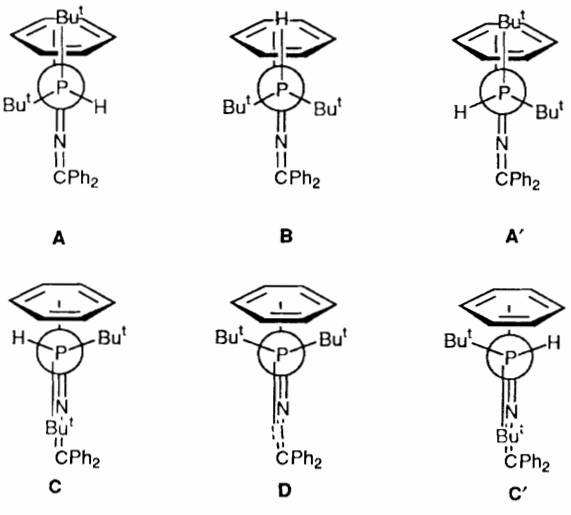


Fig. 8 Rotamers of compound **10** viewed along the Os–P axis

Experimental

All reactions were carried out under an atmosphere of argon by using Schlenk-tube techniques. The starting materials $[\{Os(C_6H_6)I_2\}_2]$ **1**,[12] $[OsI_2(C_6H_6)(PMeBu^t_2)]$ **2**,[13] $[\{OsCl_2(mes)\}_n]$ **6**[14] and $PHBu^t_2$[15] were prepared by published methods. The NMR spectra were recorded on JEOL FX 90 Q and Bruker AMX 400 spectrometers (s = singlet, d = doublet, t = triplet, spt = septet, m = multiplet, br = broadened signal), and IR spectra on a Perkin-Elmer 1420 spectrometer. The conductivity Λ was measured in nitromethane with a Schott Konduktometer CG 851, and decomposition points were determined by differential thermal analysis.

Preparations.—$[Os(C_6H_6)(\eta^2\text{-}ON{=}CMe_2)(PMeBu^t_2)]PF_6$ **3**. A suspension of compound **2** (232 mg, 0.34 mmol) in methanol (5 cm^3) was treated with KPF_6 (70 mg, 0.38 mmol) and $Na[ON{=}CMe_2]$ (35 mg, 0.37 mmol) and stirred for 90 min at room temperature. The solvent was removed *in vacuo*, and the residue extracted with CH_2Cl_2 (15 cm^3). The extract was brought to dryness *in vacuo*, and the residue recrystallized from CH_2Cl_2–diethyl ether to give a yellow microcrystalline solid: yield 193 mg (88%), decomp. 152 °C (Found: C, 33.60; H, 5.10; N, 2.10. Calc. for $C_{18}H_{33}F_6NOOsP_2$: C, 33.50; H, 5.15; N, 2.15%). Λ = 77 Ω^{-1} cm^2 mol^{-1}. NMR: ^1H (90 MHz) (CD_3NO_2, 25 °C), δ 6.23 (s, 6 H, C_6H_6), 2.17 (s, 6 H, $N{=}CCH_3$), 1.29 and 1.26 [both d, J(PH) = 13.8, 18 H, $PCCH_3$] and 1.02 [br d, J(PH) = 8.9, 3 H, PCH_3]; (CD_3NO_2, 65 °C), δ 6.25 (s, 6 H, C_6H_6), 2.14 (s, 6 H, $N{=}CCH_3$), 1.27 and 1.25 [both d, J(PH) = 13.8, 18 H, $PCCH_3$] and 1.01 [d, J(PH) = 9.1, 3 H, PCH_3]; (CD_2Cl_2, 25 °C), δ 6.11 (s, 6 H, C_6H_6), 2.16 and 2.12 (both s, 6 H, $N{=}CCH_3$), 1.25 and 1.21 [both d, J(PH) = 13.9, 18 H, $PCCH_3$] and 0.84 [br d, J(PH) = 8.8, 3 H, PCH_3]; (CD_2Cl_2, −65 °C), δ 6.11 (s, 6 H, C_6H_6), 2.13 and 2.05 (both s, 6 H, $N{=}CCH_3$), 1.23 and 1.19 [both d, J(PH) = 13.9, 18 H, $PCCH_3$] and 0.83 [d, J(PH) = 9.0, 3 H, PCH_3]; ^{31}P (36.2 MHz) (CD_3NO_2, 25 °C), δ 24.10 (s, br, $PMeBu^t_2$) and −144.58 [spt, J(PF) = 706.9, PF_6]; (CD_3NO_2, 65 °C), δ 23.95 (br s, $PMeBu^t_2$) and −144.23 [spt, J(PF) = 708.3, PF_6]; (CD_2Cl_2, 25 °C), δ 23.37 (br s, $PMeBu^t_2$) and −144.37 [spt, J(PF) = 707.4, PF_6]; (CD_2Cl_2, −65 °C), δ 27.24 (s, $PMeBu^t_2$, major rotamer), 10.16 (s, $PMeBu^t_2$, minor rotamer) and −144.37 [spt, J(PF) = 707.4 Hz, PF_6].

$[Os(C_6H_6)(=N{=}CPh_2)(PMeBu^t_2)]PF_6$ **4**. A solution of compound **3** (129 mg, 0.20 mmol) in CH_2Cl_2 (10 cm^3) was treated with $HN{=}NPh_2$ (100 μl, 0.60 mmol) and stirred for 1 h at room temperature. It was concentrated *in vacuo* to *ca.* 3 cm^3,

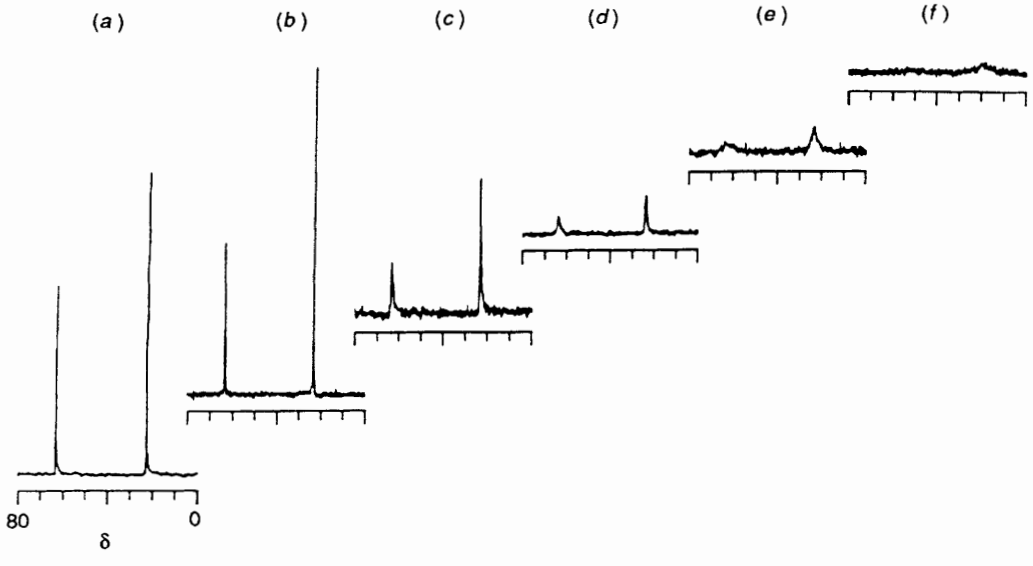


Fig. 9 The ^{31}P NMR spectra (36.2 MHz) of compound **8** in CD_3NO_2 at various temperatures (see Fig. 6)

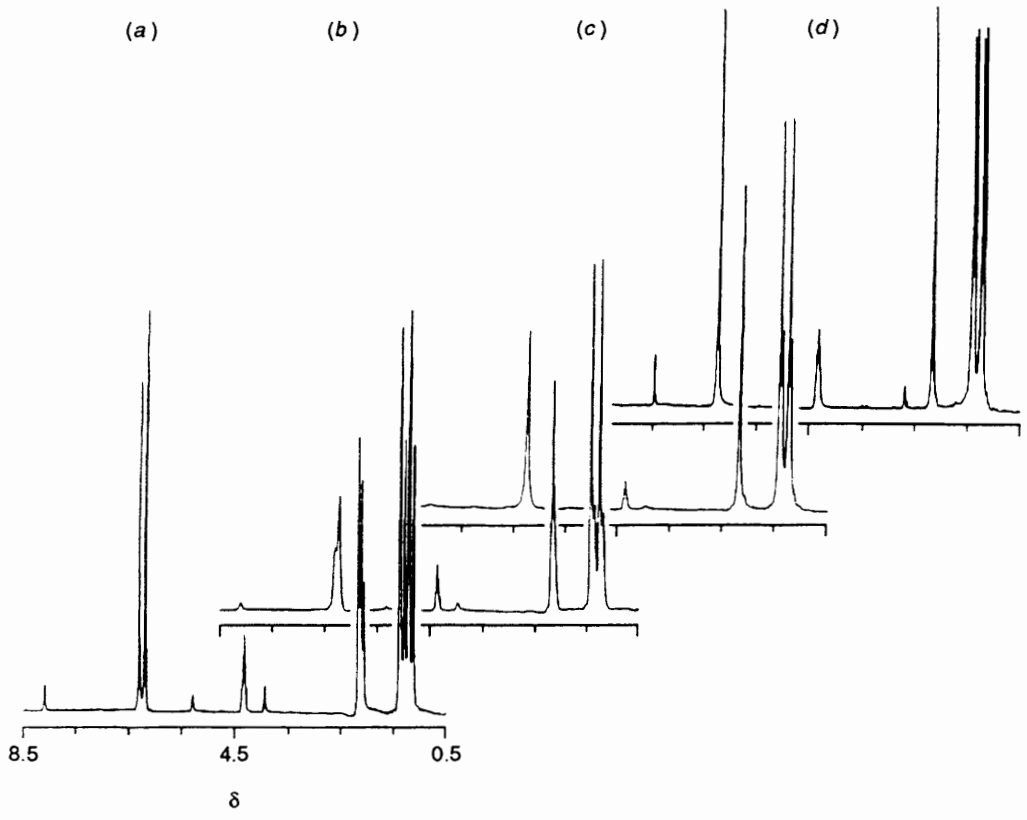


Fig. 10 Proton NMR spectra (90 MHz) of compound **8** in CD_3NO_2 at various temperatures (see Fig. 7)

and then ether (25 cm^3) was added. After standing for 12 h, an orange crystalline precipitate was formed which was identified spectroscopically by comparison with an authentic sample.[3] Yield 137 mg (91%).

$[OsI_2(C_6H_6)(PHBu^t_2)]$ **5**. A suspension of compound **1** (990 mg, 0.95 mmol) in toluene (5 cm^3) was treated with $PHBu^t_2$ (1 cm^3, 5.47 mmol) and stirred for 4 h at 90 °C. After cooling to room temperature the solvent was removed and the residue extracted with CH_2Cl_2 (40 cm^3). The extract was filtered, the filtrate was concentrated *in vacuo* to *ca.* 10 cm^3, and pentane (40 cm^3) was added. The orange solid precipitated was filtered off, repeatedly washed with pentane and dried *in vacuo*; yield 1.19 g (94%), decomp. 188 °C (Found: C, 25.45; H, 3.85. Calc. for $C_{14}H_{25}I_2OsP$: C, 25.15; H, 3.75%). IR (KBr): ν(PH) 2305 cm^{-1}. NMR: ^1H (CD_2Cl_2, 90 MHz) (25 °C), δ 6.57 [br d, J(PH) = 366, 1 H, PH], 5.98 [d, J(PH) = 0.6, 6 H, C_6H_6] and 1.53 [d, J(PH) = 13.8, 18 H, $PCCH_3$]; (−70 °C), major rotamer, δ 6.63 [br d, J(PH) = 377, PH], 6.03 (s, C_6H_6) and 1.47 [d, J(PH) = 13.7, $PCCH_3$]; minor rotamer, δ 6.54 [br d, J(PH) = 337, PH], 5.87 (s, C_6H_6) and 1.46 [d, J(PH) = 13.7 Hz, $PCCH_3$]; ^{31}P (CD_2Cl_2, 36.2 MHz) (25 °C), δ 13.70 (br s; br d in off-resonance); (−80 °C), δ 16.65 (s; d in off-resonance, major rotamer) and −0.96 (s; d in off-resonance, minor rotamer).

$[OsCl_2(mes)(PHBu^t_2)]$ **7**. This compound was prepared as described for **5**, using **6** (955 mg, 1.25 mmol for n = 2) and $PHBu^t_2$ (0.6 cm^3, 3.28 mmol) as starting materials. An orange microcrystalline solid was obtained: yield 1.15 g (87%), decomp. 202 °C (Found: C, 38.80; H, 6.05. Calc. for $C_{17}H_{31}Cl_2OsP$: C, 38.70; H, 5.90%). IR (KBr): ν(PH) 2330 cm^{-1}. NMR: ^1H ($CDCl_3$, 90 MHz, 25 °C), δ 5.69 [br d, J(PH) = 335, 1 H, PH], 5.25 (s, 3 H, $C_6H_3Me_3$), 2.12 (s, 9 H, $C_6H_3Me_3$) and 1.45 [d, J(PH) = 14.0 Hz, 18 H, $PCCH_3$]; ^{31}P (CD_2Cl_2, 36.2 MHz) (25 °C), δ 18.65 (br s; br d in off-resonance); (−35 °C), δ 18.28 (s; d in off-resonance).

$[Os(C_6H_6)(\eta^2\text{-}ON{=}CMe_2)(PHBu^t_2)]PF_6$ **8**. This compound was prepared as described for **3**, using **5** (167 mg, 0.25 mmol), KPF_6 (50 mg, 0.27 mmol) and $Na[ON{=}CMe_2]$ (25 mg, 0.26 mmol) as starting materials. A yellow crystalline solid was obtained: yield 124 mg (79%), decomp. 164 °C (Found: C, 32.45; H, 5.15; N, 2.35. Calc. for $C_{17}H_{31}F_6NOOsP_2$: C, 32.35; H, 4.95; N, 2.20%). Λ = 83 Ω^{-1} cm^2 mol^{-1}. IR (KBr): ν(PH) 2335 cm^{-1}. NMR (CD_3NO_2): ^1H (90 MHz) (25 °C), major rotamer, δ 6.19 (br s, C_6H_6), 5.97 [br d, J(PH) = 366, PH], 2.17 (br s, $N{=}CCH_3$) and 1.36 [br d, J(PH) = 14.9, $PCCH_3$]; minor rotamer, δ 6.19 (br s, C_6H_6), 2.17 (br s, $N{=}CCH_3$), 1.31 [br d, J(PH) = 15.0, $PCCH_3$], signal of PH not exactly located; (75 °C), δ 6.21 (s, 6 H, C_6H_6), 2.21 (s, 6 H, $N{=}CCH_3$), 1.40 and 1.36 [both d, J(PH) = 14.9, 18 H, $PCCH_3$], signal of PH not observed; (−25 °C), major rotamer, δ 6.15 (s, C_6H_6), 5.96 [d, J(PH) = 365, PH], 2.21 and 2.15 (both s, $N{=}CCH_3$), 1.35 and 1.33 [both, d, J(PH) = 15.0, $PCCH_3$]; minor rotamer, δ 6.26 (s, C_6H_6), 3.22 [d, J(PH) = 362.3, PH], 2.17 and 2.11 (both s, $N{=}CCH_3$) and 1.25 [d, J(PH) = 14.9, $PCCH_3$]; ^{31}P NMR (36.2 MHz) (25 °C), δ 63.32 (br s; br d in off-resonance; $PHBu^t_2$, minor rotamer), 23.85 (br s; br d in off-resonance; $PHBu^t_2$, major rotamer) and −144.42 [spt, J(PF) = 707.1, PF_6); (75 °C), δ 63.45 (br s; br d in off-resonance; $PHBu^t_2$, minor rotamer), 24.03 (br s; br d in off-resonance; $PHBu^t_2$, major rotamer) and −144.44 [spt, J(PF) = 706.9, PF_6]; (−25 °C), δ 63.22 (s; d in off-resonance; $PHBu^t_2$, minor rotamer), 23.85 (s; d in off-resonance; $PHBu^t_2$, major rotamer) and −144.45 [spt, J(PF) = 707.5 Hz, PF_6].

$[Os(mes)(\eta^2\text{-}ON{=}CMe_2)(PHBu^t_2)]PF_6$ **9**. This compound was prepared as described for **3**, using **7** (258 mg, 0.49 mmol), KPF_6 (100 mg, 0.54 mmol) and $Na[ON{=}CMe_2]$ (50 mg, 0.53 mmol) as starting materials. A yellow crystalline solid was obtained: yield 312 mg (95%); decomp. 166 °C (Found: C, 35.95; H, 5.75; N, 1.95. Calc. for $C_{20}H_{37}F_6NOOsP_2$: C, 35.65; H, 5.55; N, 2.10%). Λ = 77 Ω^{-1} cm^2 mol^{-1}. IR (KBr): ν(PH) 2365 cm^{-1}. NMR (CD_3NO_2): ^1H (90 MHz, 25 °C), δ 5.71 (s, 3 H, $C_6H_3Me_3$), 5.52 [d, J(PH) = 354.4, 1 H, PH], 2.37 [d, J(PH) = 1.0, 9 H, $C_6H_3Me_3$], 2.23 and 2.17 (both s, 6 H, $N{=}CCH_3$), 1.34 and 1.31 [both d, J(PH) = 14.6, 18 H, $PCCH_3$]; ^{13}C NMR (22.5 MHz, 25 °C), δ 145.06 (s, N=C), 98.19 [d, J(PC) = 2.2,

CCH_3 of mes], 76.39 [d, J(PC) = 2.9, CH of mes], 35.18 [d, J(PC) = 22.7, $PCCH_3$], 33.80 [d, J(PC) = 22.0, $PCCH_3$], 32.45 [d, J(PC) = 3.7, $PCCH_3$], 31.78 [d, J(PC) = 4.4, $PCCH_3$], 21.83 (s, N=CCH_3), 19.62 (s, CCH_3 of mes) and 19.07 (s, N=CCH_3). ^{31}P (36.2 MHz, 25 °C), δ 65.04 (s; d in off-resonance; $PHBu^t_2$, minor rotamer), 31.84 (s; d in off-resonance; $PHBu^t_2$, major rotamer) and −144.12 [spt, J(PF) = 707.0 Hz, PF_6].

$[Os(C_6H_6)(=N=CPh_2)(PHBu^t_2)]PF_6$ **10**. This compound was prepared as described for **4**, using **8** (385 mg, 0.61 mmol) and $HN=CPh_2$ (150 μl, 0.90 mmol) as starting materials. An orange microcrystalline solid was obtained: yield 423 mg (94%), decomp. 179 °C (Found: C, 43.95; H, 5.05; N, 1.90. Calc. for $C_{27}H_{35}F_6NOsP_2$: C, 43.85; H, 4.75; N, 1.90%). Λ = 74 Ω^{-1} cm^2 mol^{-1}. IR (KBr): ν(PH) 2315 cm^{-1}. NMR (CD_3NO_2): ^{1}H (90 MHz) (25 °C), δ 7.51 (m, 10 H, C_6H_5), 6.40 (br s, 6 H, C_6H_6), 1.23 [d, J(PH) = 15.5, 18 H, $PCCH_3$], signal of PH not exactly located; (75 °C), δ 7.51 (m, 10 H, C_6H_5), 6.40 [d, J(PH) = 0.5, 6 H, C_6H_6], 1.26 [d, J(PH) = 15.5 Hz, 18 H, $PCCH_3$], signal of PH not observed; (−25 °C), major rotamer, δ 7.52 (m, C_6H_5), 6.37 (s, C_6H_6), 6.01 [d, J(PH) = 365.8, PH] and 1.16 [d, J(PH) = 15.4, $PCCH_3$]; minor rotamer, δ 7.52 (m, C_6H_5), 6.45 (s, C_6H_6), 3.98 [d, J(PH) = 360.2, PH] and 1.25 [d, J(PH) = 15.5, $PCCH_3$]; ^{13}C (22.5 MHz, 25 °C), δ 160.32 (br s, N=C), 131.24, 130.36 and 129.52 (all s, C^{2-6} of C_6H_5), 125.12 (br s, C^1 of C_6H_5), 82.05 (br s, C_6H_6), 33.94 (br s, $PCCH_3$) and 31.36 [d, J(PC) = 4.4, $PCCH_3$]; (100.6 MHz, 25 °C), δ 159.93 (s, br, N=C), 131.27, 130.42 and 129.56 (all s, C^{2-6} of C_6H_5), 124.59 (br s, C^1 of C_6H_5), 82.50 (br s, C_6H_6, major rotamer), 80.90 (br s, C_6H_6, minor rotamer), 34.83 (br s, $PCCH_3$, minor rotamer), 32.46 (br s, $PCCH_3$, major rotamer) and 31.36 (br s, $PCCH_3$); ^{31}P (36.2 MHz) (25 °C), δ 58.17 (br s; br d in off-resonance; $PHBu^t_2$, minor rotamer), 29.12 (br s; br d in off-resonance; $PHBu^t_2$, major rotamer) and −144.42 [spt, J(PF) = 707.1, PF_6]; (75 °C), δ 58.39 (br s; br d in off-resonance; $PHBu^t_2$, minor rotamer), 29.27 (br s; br d in off-resonance; $PHBu^t_2$, major rotamer) and −144.47 [spt, J(PF) = 706.9, PF_6]; (−25 °C), δ 57.81 (s; d in off-resonance; $PHBu^t_2$, minor rotamer), 28.80 (s; d in off-resonance; $PHBu^t_2$, major rotamer) and −154.44 [spt, J(PF) = 707.3 Hz, PF_6].

$[Os(mes)(=N=CPh_2)(PHBu^t_2)]PF_6$ **11**. This compound was prepared as described for **4** using **9** (262 mg, 0.39 mmol) and $HN=CPh_2$ (100 μl, 0.60 mmol) as starting materials. An orange microcrystalline solid was obtained: yield 276 mg (91%); decomp. 205 °C (Found: C, 46.80; H, 5.40; N, 1.75. Calc. for $C_{30}H_{41}F_6NOsP_2$: C, 46.90; H, 5.30; N, 1.80%). Λ = 72 Ω^{-1} cm^2 mol^{-1}. IR (KBr): ν(PH) 2345 cm^{-1}. NMR (CD_3NO_2): ^{1}H (90 MHz, 25 °C), δ 7.50 (m, 10 H, C_6H_5), 5.59 [d, br, J(PH) = 356.3, 1 H, PH], 5.44 (s, 3 H, $C_6H_3Me_3$), 2.59 (s, 9 H, $C_6H_3Me_3$) and 1.20 [d, J(PH) = 15.3, 18 H, $PCCH_3$]; ^{13}C (22.5 MHz, 25 °C), δ 159.64 [s, J(PC) = 3.7, N=C], 130.98, 130.14 and 129.55 (all s, C^{2-6} of C_6H_5), 125.50 [d, J(PC) = 3.7, C^1 of C_6H_5], 99.59 [d, J(PC) = 2.2, CCH_3 of mes], 80.65 [d, J(PC) = 2.9, CH of mes], 34.48 [d, J(PC) = 24.9, $PCCH_3$], 31.59 [d, J(PC) = 4.4, $PCCH_3$] and 20.79 (s, CCH_3 of mes); ^{31}P (36.2 MHz, 25 °C), δ 37.90 (s; d in off-resonance; $PHBu^t_2$) and −144.42 [spt, J(PF) = 707.6 Hz, PF_6].

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