Sodium oximates as starting materials for the synthesis of half-sandwich-type arene(oximato) and arene(azavinylidene) osmium complexes [1]

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Abstract

The reaction of $[C_6H_6OsI_2(P^iPr_3)]$ (1) with $Na[ON=CR_2]$ ($R_2 = Ph_2$, Me_2, $C(CH_2)_5$) in the presence of KPF_6 leads to the formation of the oximato osmium(II) complexes $[C_6H_6Os(\eta^2-ON=CR_2)(P^iPr_3)]PF_6$ (6, 7, 8b) in almost quantitative yield. The mesitylene compounds $[(mes)Os(\eta^2-ON=CR'R'')(PR_3)]PF_6$ (9–14) have been prepared similarly using $[(mes)OsCl_2(PR_3)]$ (3–5) as starting materials. The synthesis of $[C_6H_6Os(\eta^2-ON=CMe^tBu)(P^iPr_3)]PF_6$ (17) has been achieved from $[C_6H_6OsCl_2(P^iPr_3)]$ (16) which in turn is prepared from $[C_6H_6Os(\eta^2-O_2C=O)(P^iPr_3)]$ (15) and excess Me_3SiCl. Reaction of 1, $[C_6H_6OsI_2(PMe^tBu_2)]$ (2) and 3 ($PR_3 = P^iPr_3$) with $Na[ON = CMe^tBu]$ in the presence of KPF_6, in methanol as solvent, unexpectedly yields the azavinylidene complexes $[(arene)Os(=N=CMe^tBu)(PR_3)]PF_6$ (18b, 19, 20). The X-ray structural analysis of 18b reveals the presence of a nearly linear Os–N–C fragment with an Os–N distance that is in agreement with typical osmium–nitrogen double bond lengths. Related azavinylideneosmium compounds $[(arene)Os(=N=CR'R'')(PR_3)]PF_6$ (21–26) have been obtained on treatment of the corresponding oximato complexes 7, 10 or 14 with either $HN=CR'R''$ or, for $R' = H$ and $R'' = Ph$, the trimethylsilyl derivative.

*Keywords:* Osmium; Vinylidene complexes; Oximes; Arene complexes

1. Introduction

Over the last few years we have been exploring the chemistry of d^8 azavinylidene transition-metal complexes. For osmium compounds of general composition $[(arene)Os(=N=CRR')(L)]X$ ($R,R' = $ alkyl, aryl; $L = PMe_3$, PMe^tBu_2, P^iPr_3), which were the target both for stereochemical investigations [1] and reactivity studies [2], two methods of preparation were originally used [3]. The first method employed the hydrido complex $[C_6H_6OsH(I)(PMe^tBu_2)]$ and oximes $HON=CRR'$ as starting materials and proceeds via hydrido(oxime)osmium species as intermediates, reacting with Al_2O_3 by

elimination of water to give the desired products. The second method starts with the dichloro- or diiodoosmium(II) compounds $[(arene)OsX_2(PR_3)]$, which upon treatment with imines $HN=C(R)Ph$ or their derivatives $XN=C(R)Ph$ ($X = Li$, $SiMe_3$) afford the half-sandwich-type azavinylidene complexes [3]. During attempts to prepare analogous compounds with $L = P^iPr_3$ or PH^tBu_2, we discovered that a stepwise synthesis of $[(arene)Os(=N=CRR')(L)]X$ via the oximato complexes $[(arene)Os(\eta^2-ON=CR'R'')(L)]X$ is feasible. Herein, we report in detail the preparation of arene(oximato) and arene(azavinylidene) osmium compounds, both with benzene and mesitylene as arene ligands, using sodium oximates as starting material. We also describe a new method to convert diiodo into dichloroosmium(II) complexes via the corresponding carbonates as intermediates. Some preliminary results of this work have already been communicated [4].

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[1] Dedicated to Professor Marv Rausch on the occasion of his 65th birthday in recognition of his important contributions to organometallic chemistry.
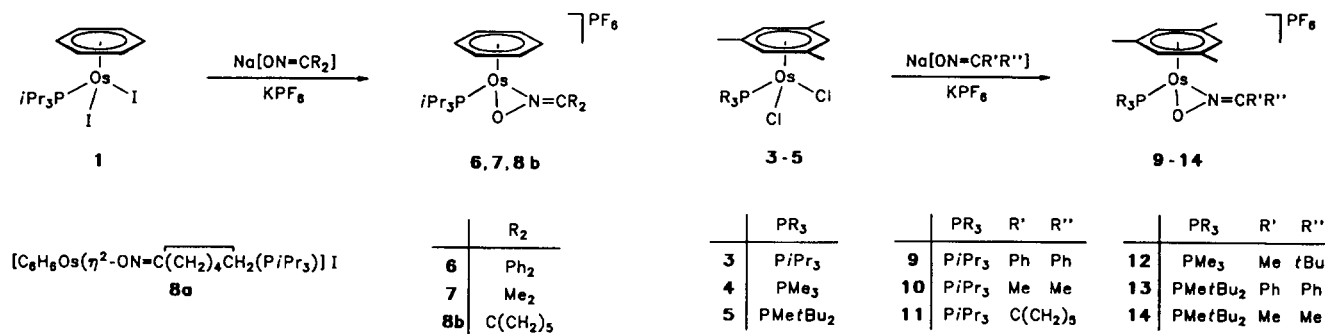
Scheme 1.

Scheme 2.

2. Results and discussion

2.1. Preparation of arene(oximato)osmium(II) complexes

Under conditions similar to those used for the preparation of the osmium azavinylidenes $[C_6H_6Os-(=N=CRPh)(PMe^tBu_2)]PF_6$ (R = Me, Ph) [3], compound 1 reacts with Na[ON=CR$_2$] and KPF$_6$ in methanol at room temperature to give the oximato complexes 6, 7 and 8b (Scheme 1) in nearly quantitative yield. The yellow crystalline solids are only slightly air-sensitive and easily soluble in polar solvents such as CH$_2$Cl$_2$ or nitromethane. The composition and piano stool-type configuration is supported by elemental analysis, by conductivity measurements, and in particular by comparison of the spectroscopic data with those of the ruthenium analogues [5]. The characteristic feature of the ^{1}H NMR and ^{13}C NMR spectra of 7 are the two signals for the oximato methyl protons and carbon atoms, indicating that the two CH$_3$ groups are stereochemically different. While attempts to prepare the iodide $[C_6H_6Os(\eta^2$-ON=CPh$_2)(P^iPr_3)]I$ from 1 and Na[ON=CPh$_2$] in methanol failed, the corresponding compound 8a was obtained from 1 and Na[ON= C(CH$_2)_4$CH$_2$].
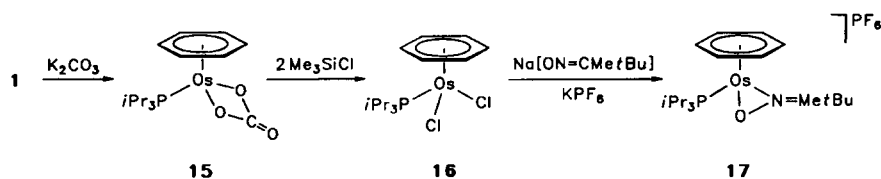
The synthesis of the mesitylene osmium complexes 9–14 is outlined in Scheme 2. The reactions of 3–5 with the oximates and KPF$_6$ are faster than those of the iodo compound 1 since the dichloro derivatives are more soluble in methanol (or acetone) than 1. The yield of 9–14 ranged from 75 to 85%. It should be mentioned that compound 12 with PMe$_3$ as the phosphine ligand is significantly less stable than the P^{i}Pr$_3$ or PMe^{t}Bu$_2$ counterparts. This phenomenon has also been observed in related ruthenium chemistry [5] and is possibly due to

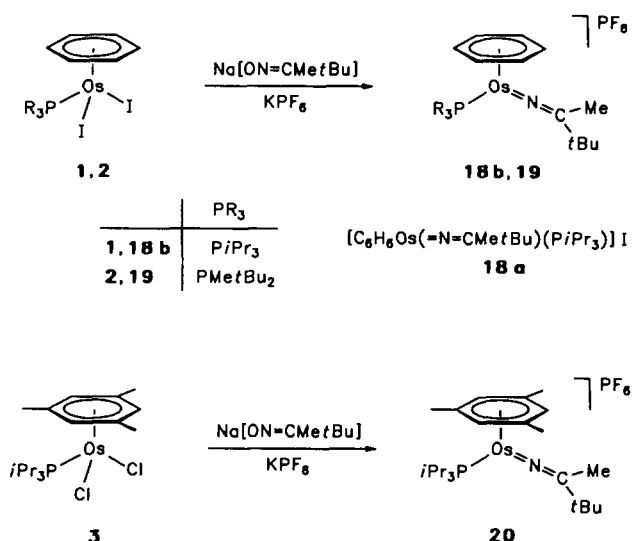the less shielded metal center in 12 which can be attacked more easily by polar solvents or other substrates.

Since the reaction of 1 with Na[ON=CMe^{t}Bu] and KPF$_6$ in methanol quite unexpectedly led to an azavinylideneosmium instead of an oximato complex (see discussion below), the synthesis of $[C_6H_6Os(\eta^2-ON=CMe^tBu)(P^iPr_3)]PF_6$ (17) was attempted via the dichloro derivative 16 as starting material. Compound 16, which had originally been prepared in our laboratory by a rather sophisticated multistep route [6], is more readily available from 1 via the carbonato complex 15 (Scheme 3). Yellow, air-stable solid 15 was chosen as an intermediate because on treatment of 1 with HCl or [NEt$_4$]Cl no halide exchange occurs. Compound 15 reacts quite smoothly with an excess of Me$_3$SiCl in CH$_2$Cl$_2$ to give the dichloroosmium(II) complex 16 in practically quantitative yield. For the conversion of 16 to the oximato derivative 17, it is important to stir the reaction mixture consisting of 16, Na[ON=CMe^{t}Bu], KPF$_6$ and acetone only for a short period of time (ca. 10 min) to avoid a secondary reaction which leads to the formation of 18b. Small amounts of 18b can be separated from 17 by fractional crystallization. At room temperature, solutions of 17 in nitromethane or chloroform are remarkably stable; even after they have been stirred for 24 h only traces of 18b can be detected.

2.2. Synthesis and structural characterization of arene(azavinylidene)osmium(0) complexes

The observation that upon treatment of 16 with Na[ON=CMe^{t}Bu], even in the absence of a reducing

Scheme 3.

Scheme 4.

Fig. 1. Molecular structure (SCHAKAL diagram) of complex 18b (hydrogen atoms omitted for clarity).

agent (or O-acceptor) an azavinylideneosmium complex is generated, encouraged further investigation of the reactivity of 1 towards the sodium oximate Na[ON=CMe^{t}Bu] under various conditions. As mentioned in the introduction, we had previously shown that compounds of general composition [(arene)Os-(=N=CRR')(L)]X can be prepared either from [(arene) OsH(I)(L)] and oximes or from [(arene)OsX$_2$(L)] and imines [3], but use of the easily-to-handle sodium oximates as starting materials would certainly be an advantage. Indeed, in methanol solution, compound 1 reacts with Na[ON=CMe^{t}Bu] to give the azavinylidene complex 18a, albeit in unsatisfactory quantities. However, treatment of compound 1 with Na[ON=CMe^{t}Bu] in the presence of KPF$_6$, yields the corresponding PF$_6$ salt 18b in ca. 70% yield (Scheme 4). NMR spectroscopic studies of the reaction mixture confirmed that the oximato derivative 17 is formed as an intermediate. Despite extensive investigations concerning potential oxygen acceptor reagents in the reaction mixture we were unfortunately not able to unambiguously establish this aspect of the aforementioned transformation.

The synthesis of 19 and 20 proceeds analogously to that of 18b. In contrast to the oximatoosmium compounds 6–14 which are yellow, the azavinylidene complexes 18–20 are orange solids which are moderately air-sensitive and should be stored under argon below 0°C. The most typical feature in the ^{13}C NMR spectra of 18b and 20 is the appearance of a low-field signal at δ ca. 165 which is assigned to the carbon atom of the Os=N=C unit.

Fig. 1 shows the result of the X-ray crystal structural analysis of 18b. There are three independent molecules in the unit cell. From molecules 1 and 2, all non-hydrogen atoms with the exception of the phenyl carbon atoms were refined anisotropically; from molecule 3 only the Os, N, P and F atoms (owing to the high number of parameters) were refined anisotropically. The cation contains a nearly trigonal planar coordinated metal atom with the midpoint of the benzene ring at one edge of the plane; this corresponds structurally to the vinylidenerhodium complex [C$_5$H$_5$Rh(=C=CHPh)(P-^{i}Pr$_3$)] [7]. The Os–N–Cl chain is almost linear and forms a plane with C2 and C6 perpendicular (angle 89.1(7) or 90.0(8)° respectively) to the best plane of P1,

Table 1
Selected intramolecular bond distances (Å) and bond angles (deg) in complex 18b, with esds; there are three independent molecules: molecule 1, atoms without star; molecule 2, atoms with one star; molecule 3, atoms with two stars in the unit cell

Os–M	1.73(1)	Os*–M*	1.75(1)	Os**–M**	1.73(1)
Os–P1	2.371(5)	Os*–P1*	2.373(3)	Os**–P1**	2.363(5)
Os–N	1.81(2)	Os*–N*	1.83(2)	Os**–Cl**	1.81(2)
N–Cl	1.32(3)	N*–Cl*	1.29(3)	N**–Cl**	1.52(5)
Cl–C2	1.40(3)	Cl*–C2*	1.35(3)	Cl**–C2**	1.36(6)
Cl–C6	1.53(4)	Cl*–C6*	1.57(4)	Cl**–C6**	1.34(5)
P1–Os–N	88.8(7)	P1*–Os*–N*	89.3(6)	P1**–Os**–N**	91.7(8)
N–Cl–C2	124 (2)	N*–Cl*–C2*	128 (3)	N**–Cl**–C2**	105 (3)
C2–Cl–C6	112 (2)	C2*–Cl*–C6*	110 (2)	C2**–Cl**–C6**	125 (4)
Os–N–Cl	167 (2)	Os*–N*–Cl*	168 (2)	Os**–N**–Cl**	155 (2)
N–Cl–C6	122 (2)	N*–Cl*–C6*	122 (2)	N**–Cl**–C6**	130 (4)

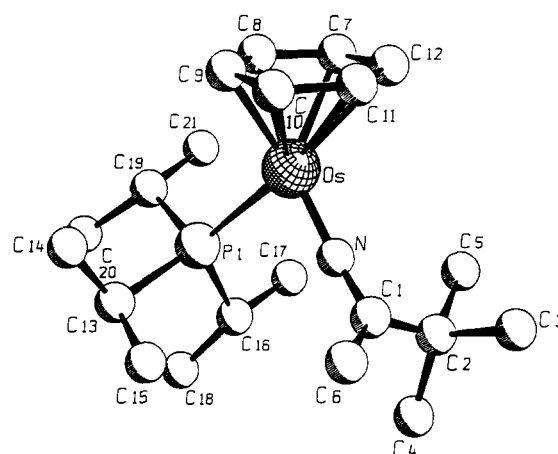M, M* and M** are defined as the midpoints of the benzene rings.

Os and the midpoint of the benzene ring. The orthogonality is consistent with the formation of a $d_\pi p_\pi$ bond between osmium and nitrogen and also explains the short Os–N distance of 1.81(2) or 1.83(2) Å (Table 1). A value of 2.074(5) Å (2.091(5) Å) is found for the Os–N single bond in [(mes)Os{κ^2(N,C)–NHC(Ph)C$_6$-H$_4$}(P^{i}Pr$_3$)]PF$_6$ [2], a metallaheterocycle obtained on protonation of [(mes)Os(=N=CPh$_2$)(P^{i}Pr$_3$)]PF$_6$ with CF$_3$CO$_2$H. The N–C1 distance in **18b** is similar to that in other azavinylidene transition-metal complexes [8] and also agrees with the N–C-bond lengths found in 2-azaallenium ions [9].

A second preparative route to azavinylideneosmium-(0) compounds of the half-sandwich type was discovered during investigations of the reactivity of the oximato derivatives **7** and **10**. While treatment of **7** with Me$_3$SiN=CHPh or reaction of **7** and **10** with HN=CEtPh resulted in the displacement of the oxime and formation of the corresponding cationic species containing either an Os=N=CHPh or Os=N=CEtPh unit (Scheme 5), the reaction of **7** with HN=CMe(OEt) leads to the formation of **23**. Obviously, the iminoester is able to abstract an oxygen atom from the oximato ligand and thus generates a compound with an Os=N=CMe$_2$ moiety that is not accessible from one of the previously established routes [3]. Attempts to perform a similar oxygen abstraction from **7** or **10** with PPh$_3$ or PMe$_3$ failed and led only to trace amounts of the azavinylidene complex. The mesityleneosmium compounds **25** and **26** containing PMe^{t}Bu$_2$ as the phosphine ligand could also be prepared by ON=CMe$_2$/N=CRPh exchange (Scheme 6) and have been isolated in excellent yields. The formation of free oxime HON=CMe$_2$ in the reaction of **14** with HN=CPh$_2$ has been demonstrated by NMR measurements.

We note that in the ^{1}H and ^{13}C NMR spectra of **22**,

	R
25	Ph
26	Et
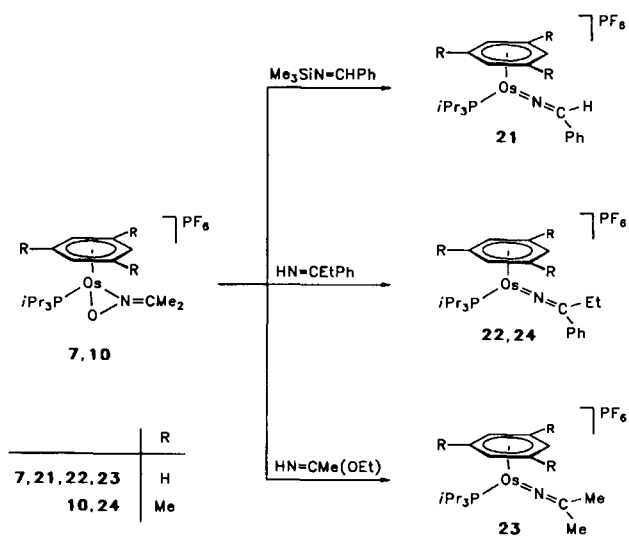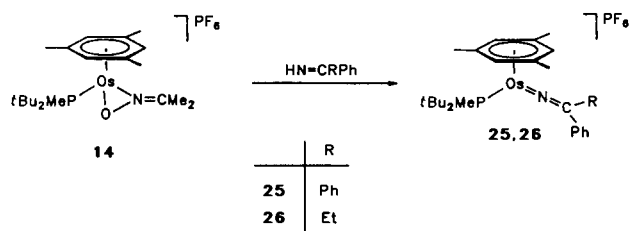
Scheme 6.

24 and **26** two signals for the PCHCH$_3$ or PCCH$_3$ methyl protons and the respective carbon atoms are observed, indicating that the isopropyl-CH$_3$ and tert-butyl-CH$_3$ groups are diastereotopic. The conclusion is that the plane of the N=C, ipso-C(phenyl) and CH$_2$ carbon atoms of the azavinylidene ligand is perpendicular to the plane formed by Os, P and the midpoint of the arene ring, as found in the X-ray structure of **18b**. The allene-like geometry is also supported by the appearance of two signals for the CH$_2$ protons of the C-bonded ethyl group which give rise to an AB pattern in the ^{1}H NMR spectra of **22** and **26**. Even on warming to 80°C in CD$_3$NO$_2$, no broadening of the two signals of the methylene protons could be observed.

3. Experimental section

All reactions were carried out under argon and in carefully dried solvents. The starting materials [C$_6$H$_6$OsI$_2$(P^{i}Pr$_3$)] (1) [10], [C$_6$H$_6$OsI$_2$(PMe^{t}Bu$_2$)] (2) [11], [(mes)OsCl$_2$(P^{i}Pr$_3$)] (3) [12], [(mes)OsCl$_2$(PMe$_3$)] (4) [13] and [(mes)OsCl$_2$(PMe^{t}Bu$_2$)] (5) [12] were prepared by known methods. IR: Perkin–Elmer 1420; NMR: Varian EM 360 L, Jeol FX 90 Q, Bruker AC 200. Equivalent conductivity Λ, was measured in nitromethane. Melting and decomposition points were determined by DTA.

3.1. Preparation of [C$_6$H$_6$Os(η^2-ON=CPh$_2$)(P^{i}Pr$_3$)]-PF$_6$ (6)

A suspension of 213 mg (0.31 mmol) of **1** in 5 ml of methanol was treated with 60 mg (0.33 mmol) of KPF$_6$ and 70 mg (0.32 mmol) of Na[ON=CPh$_2$] and the mixture was stirred for 90 min at room temperature. The solvent was removed in vacuo, the residue was extracted with 15 ml of CH$_2$Cl$_2$, and the extract was brought to dryness in vacuo. After recrystallization from CH$_2$Cl$_2$–Et$_2$O, a yellow microcrystalline solid was obtained. Yield 208 mg (87%); dec. temp. 135°C; Λ = 81 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 44.23; H, 4.87; N, 1.86. C$_{28}$H$_{37}$F$_6$NOOsP$_2$. Calc.: C, 43.69; H, 4.84; N, 1.82%. ^{1}H NMR (200 MHz, CD$_3$NO$_2$): δ 7.59 (m; 10H; C$_6$H$_5$), 6.35 (s; 6H; C$_6$H$_6$), 2.37 (m; 3H;

	R
7,21,22,23	H
10,24	Me

Scheme 5.

PCHCH$_3$), 1.25 (dd; J(PH) = 13.7, J(HH) = 6.7 Hz; 9H; PCHCH_3), 1.15 (dd, J(PH) = 14.0, J(HH) = 7.0 Hz; 9H; PCHCH_3). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 23.60 (s; P^{i}Pr$_3$), -144.48 (sept; J(PF) = 706.7 Hz; PF$_6$).

3.2. Preparation of [C$_6$H$_6$Os(η^2-ON=CMe$_2$)(P^{i}Pr$_3$)]-PF$_6$ (7)

Compound 7 was prepared as described for 6 starting from 307 mg (0.45 mmol) of 1, 90 mg (0.49 mmol) of KPF$_6$ and 50 mg (0.53 mmol) of Na[ON=CMe$_2$]. Yellow crystals were isolated. Yield 267 mg (92%); dec. temp. 144°C; Λ = 73 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 33.36; H, 5.03; N, 2.06. C$_{18}$H$_{33}$F$_6$NOOsP$_2$. Calc.: C, 33.49; H, 5.15; N, 2.17%. ^{1}H NMR (200 MHz, CD$_3$NO$_2$): δ 6.22 (s; 6H; C$_6$H$_6$), 2.30 (m; 3H; PCHCH$_3$), 2.19 and 2.14 (both s; 3H each; N=CCH$_3$), 1.22 and 1.21 (both dd; J(PH) = 14.0, J(HH) = 7.1 Hz; 9H each; PCHCH_3). ^{13}C NMR (50.3 MHz, CD$_3$NO$_2$): δ 144.31 (s; N=C), 78.77 (d; J(PC) = 2.5 Hz; C$_6$H$_6$), 25.50 (d; J(PC) = 28.2 Hz; PCHCH$_3$), 21.96 (s; N=CCH$_3$), 20.11 (s; PCHCH$_3$), 19.74 (s; N=CCH$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 22.74 (s; P^{i}Pr$_3$), -145.48 (sept; J(PF) = 706.9 Hz; PF$_6$).

3.3. Preparation of [C$_6$H$_6$Os(η^2-ON=$\overline{C(CH_2)_4C}$H$_2$)-(P^{i}Pr$_3$)]I (8a)

A suspension of 122 mg (0.18 mmol) of 1 in 5 ml of methanol was treated with 30 mg (0.22 mmol) of Na[ON=$\overline{C(CH_2)_4C}$H$_2$] and the mixture was stirred for 30 min at room temperature. After the solvent had been removed, the residue was worked up as described for 6. A yellow microcrystalline solid was isolated. Yield 96 mg (80%); dec. temp. 102°C; Λ = 68 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 37.09; H, 5.56; N, 1.99. C$_{21}$H$_{37}$IN-OOsP. Calc.: C, 37.78; H, 5.59; N, 2.10%. ^{1}H NMR (60 MHz, CD$_3$NO$_2$): δ 6.23 (s; 6H; C$_6$H$_6$), 2.61 (m; 4H; C(CH$_2$)$_5$), 2.43 (m; 3H; PCHCH$_3$), 1.67 (m; 6H; C(CH$_2$)$_5$), 1.23 (dd; J(PH) = 13.9, J(HH) = 6.8 Hz; 18H; PCHCH_3). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 22.50 (s).

3.4. Preparation of [C$_6$H$_6$Os(η^2-ON=$\overline{C(CH_2)_4C}$H$_2$)(P-^{i}Pr$_3$)]PF$_6$ (8b)

Compound 8b was prepared as described for 6 starting from 345 mg (0.51 mmol) of 1, 100 mg (0.54 mmol) of KPF$_6$ and 70 mg (0.52 mmol) of Na[ON=$\overline{C(CH_2)_4C}$H$_2$]. A yellow powder was isolated. Yield 317 mg (91%); dec. temp. 95°C; Λ = 76 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 37.24; H, 5.42; N, 1.93. C$_{21}$H$_{37}$F$_6$NOOsP$_2$. Calc.: C, 36.79; H, 5.44; N, 2.04%. ^{1}H NMR (60 MHz, CD$_3$NO$_2$): δ 6.19 (s; 6H; C$_6$H$_6$), 2.60 (m; 4H; C(CH$_2$)$_5$), 2.30 (m; 3H; PCHCH$_3$), 1.67 (m; 6H; C(CH$_2$)$_5$), 1.25 and 1.22 (both dd; J(PH) =

14.0, J(HH) = 7.1 Hz; 9H each; PCHCH_3). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 22.54 (s; P^{i}Pr$_3$), -145.48 (sept; J(PF) = 706.4 Hz; PF$_6$).

3.5. Preparation of [(mes)Os(η^2-ON=CPh$_2$)(P^{i}Pr$_3$)]-PF$_6$ (9)

Compound 9 was prepared as described for 6 starting from 107 mg (0.20 mmol) of 3, 40 mg (0.22 mmol) of KPF$_6$ and 50 mg (0.23 mmol) of Na[ON=CPh$_2$]. The reaction time was 30 min. A yellow microcrystalline solid was obtained. Yield 123 mg (76%); dec. temp. 143°C; Λ = 86 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 45.89; H, 5.19; N, 1.67. C$_{31}$H$_{43}$F$_6$NOOsP$_2$. Calc.: C, 45.87; H, 5.34; N, 1.73%. ^{1}H NMR (90 MHz, CD$_3$NO$_2$): δ 7.94 and 7.54 (both m; 10H; C$_6$H$_5$), 6.05 (s; 3H; C$_6$H$_3$Me$_3$), 2.43 (m; 3H; PCHCH$_3$), 2.40 (s; 9H; C$_6$H$_3$Me$_3$), 1.28 and 1.27 (both dd; J(PH) = 14.0, J(HH) = 7.1 Hz; 9H each; PCHCH_3). ^{13}C NMR (22.5 MHz, CD$_3$NO$_2$): δ 143.44 (s; N=C), 134.40, 134.04, 132.22, 131.47, 130.23, 130.01, 129.88 and 129.42 (all s; C$_6$H$_5$), 96.14 (d; J(PC) = 2.2 Hz; CCH$_3$ of mes), 78.83 (d; J(PC) = 2.9 Hz; CH of mes), 25.36 (d; J(PC) = 27.1 Hz; PCHCH$_3$), 20.40 (s; CCH$_3$ of mes), 19.82 (s; PCHCH$_3$), 19.43 (d; J(PC) = 1.5 Hz; PCHCH$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 19.61 (s; P^{i}Pr$_3$), -144.60 (sept; J(PF) = 707.1 Hz; PF$_6$).

3.6. Preparation of [(mes)Os(η^2-ON=CMe$_2$)(P^{i}Pr$_3$)]-PF$_6$ (10)

Compound 10 was prepared as described for 6 starting from 157 mg (0.29 mmol) of 3, 55 mg (0.30 mmol) of KPF$_6$ and 30 mg (0.32 mmol) of Na[ON=CMe$_2$]. The reaction time was 30 min. In this reaction, acetone can be used as solvent instead of methanol. After recrystallization from CH$_2$Cl$_2$–Et$_2$O yellow crystals were obtained. Yield 168 mg (84%); dec. temp. 140°C; Λ = 76 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 36.97; H, 6.02; N, 2.05. C$_{21}$H$_{39}$F$_6$NOOsP$_2$. Calc.: C, 36.68; H, 5.72; N, 2.04%. ^{1}H NMR (60 MHz, CD$_3$NO$_2$): δ 5.80 (s; 3H; C$_6$H$_3$Me$_3$), 2.45 (s; 9H; C$_6$H$_3$Me$_3$), 2.28 (m; 3H; PCHCH$_3$), 2.13 and 2.03 (both s; 3 H each; N=CCH$_3$), 1.22 (dd; J(PH) = 13.9, J(HH) = 6.9 Hz; 18H; PCHCH_3). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 20.03 (s; P^{i}Pr$_3$), -145.53 (sept; J(PF) = 707.1 Hz; PF$_6$).

3.7. Preparation of [(mes)Os(η^2-ON=$\overline{C(CH_2)_4C}$H$_2$)-(P^{i}Pr$_3$)]PF$_6$ (11)

Compound 11 was prepared as described for 6 starting from 135 mg (0.25 mmol) of 3, 50 mg (0.27 mmol) of KPF$_6$ and 35 mg (0.26 mmol) of Na[ON=$\overline{C(CH_2)_4C}$H$_2$]. The reaction time was 30 min. A yellow microcrystalline solid was obtained. Yield 149

mg (82%); dec. temp. 140°C; $A = 74$ cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 39.71; H, 5.95; N, 1.94. $C_{24}H_{43}F_6NOOsP_2$. Calc.: C, 39.61; H, 5.96; N, 1.92%. ^{1}H NMR (90 MHz, CD$_3$NO$_2$): δ 5.85 (s; 3H; $C_6H_3Me_3$), 2.53 (m; 4H; C(CH$_2$)$_5$), 2.44 (s; 9H; $C_6H_3Me_3$), 2.23 (m; 3H; PCHCH$_3$), 1.69 (m; 6H; C(CH$_2$)$_5$), 1.25 (dd; J(PH) = 13.9, J(HH) = 7.0 Hz; 18H; PCHCH_3). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 19.79 (s; P^{i}Pr$_3$), −145.57 (sept; J(PF) = 707.0 Hz; PF$_6$).

3.8. Preparation of [(mes)Os(η²-ON= CMe'Bu)-(PMe₃)]PF₆ (12)

A solution of 160 mg (0.35 mmol) of **4** in 5 ml of methanol was treated with 70 mg (0.38 mmol) of KPF$_6$ and 55 mg (0.40 mmol) of Na[ON=CMe^{t}Bu] and the reaction mixture was stirred for 30 min at room temperature. The solvent was removed, the residue was extracted with 20 ml of CH$_2$Cl$_2$, and the extract was concentrated to ca. 1 ml in vacuo. The resulting concentrate was chromatographed on Al$_2$O$_3$ (neutral, activity grade V, 2 cm column). A yellow fraction was eluted with CH$_2$Cl$_2$ and brought to dryness in vacuo. After recrystallization from CH$_2$Cl$_2$–Et$_2$O, a yellow microcrystalline solid was obtained. Yield 162 mg (72%); dec. temp. 105°C; $A = 78$ cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 33.18; H, 5.22; N, 2.14. $C_{18}H_{33}F_6NOOsP_2$. Calc.: C, 33.49; H, 5.15; N, 2.17%. ^{1}H NMR (60 MHz, CD$_3$NO$_2$): δ 5.90 (s; 3H; $C_6H_3Me_3$), 2.38 (s; 9H; $C_6H_3Me_3$), 2.18 (s; 3H; N=CCH$_3$), 1.40 (d; J(PH) = 10.7 Hz; 9H; PCH$_3$), 1.28 (s; 9H; N=CC(CH$_3$)$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ −29.71 (s; PMe$_3$), −144.42 (sept; J(PF) = 707.1 Hz; PF$_6$).

3.9. Preparation of [(mes)Os(η²-ON= CPh₂)(PMe-'Bu₂)]PF₆ (13)

Compound **13** was prepared as described for **6** starting from 165 mg (0.31 mmol) of **5**, 60 mg (0.33 mmol) of KPF$_6$ and 75 mg (0.35 mmol) of Na[ON=CPh$_2$]. The reaction time was 1 h. A brownish-yellow microcrystalline solid was obtained. Yield 201 mg (80%); dec. temp. 141°C; $A = 75$ cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 45.60; H, 5.27; N, 2.01. $C_{31}H_{43}F_6NOOsP_2$. Calc.: C, 45.86; H, 5.33; N, 1.73%. ^{1}H NMR (90 MHz, CD$_3$NO$_2$): δ 7.60 (m; 10H; C_6H_5), 6.17 (s; 3H; $C_6H_3Me_3$), 2.35 (s; 9H; $C_6H_3Me_3$), 1.79 (d; J(PH) = 8.5 Hz; 3H; PCH$_3$), 1.26 and 1.22 (both d; J(PH) = 13.8 Hz; 9H each; PCCH$_3$).

3.10. Preparation of [(mes)Os(η²-ON= CMe₂)(PMe-'Bu₂)]PF₆ (14)

Compound **14** was prepared as described for **6** starting from 163 mg (0.30 mmol) of **5**, 60 mg (0.33 mmol) of KPF$_6$ and 34 mg (0.35 mmol) of Na[ON=CMe$_2$].

The reaction time was 1 h. A brownish-yellow microcrystalline solid was obtained. Yield 183 mg (86%); dec. temp. 135°C; $A = 78$ cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 36.99; H, 5.73; N, 2.25. $C_{21}H_{39}F_6NOOsP_2$. Calc.: C, 36.67; H, 5.71; N, 2.04%. ^{1}H NMR (90 MHz, CD$_3$NO$_2$): δ 5.98 (s; 3H; $C_6H_3Me_3$), 2.38 (s; 9H; $C_6H_3Me_3$), 2.23 and 2.18 (both s; 3H each; N=CCH$_3$), 1.78 (d; J(PH) = 8.3 Hz; 3H; PCH$_3$), 1.24 and 1.19 (both d; J(PH) = 13.7 Hz; 9H each; PCCH$_3$).

3.11. Preparation of [C₆H₆Os(η²-O₂C= O)(P'Pr₃)] (15)

A suspension of 273 mg (0.40 mmol) of **1** in 5 ml of methanol was treated with 60 mg (0.43 mmol) of K$_2$CO$_3$ and stirred for 1 h at room temperature. The solvent was removed, the residue extracted with 20 ml of CH$_2$Cl$_2$, and the extract brought to dryness in vacuo. After recrystallization from CH$_2$Cl$_2$–pentane, a yellow microcrystalline solid was obtained. Yield 183 mg (94%); m.p. 122°C (dec.). Anal. Found: C, 39.08; H, 5.73. $C_{16}H_{27}O_3OsP$. Calc.: C, 39.33; H, 5.57%. Mol. weight Found: 452 (in CH$_2$Cl$_2$); Calc.: 488.6. IR (KBr) ν(C=O) 1655 and 1630 cm^{-1}. ^{1}H NMR (60 MHz, CDCl$_3$): δ5.88 (s; 6H; C_6H_6), 2.40 (m; 3H; PCHCH$_3$), 1.29 (dd; J(PH) = 13.6, J(HH) = 6.9 Hz; 18H; PCHCH_3). ^{13}C NMR (22.5 MHz, CDCl$_3$): δ 168.19 (d; J(PC) = 2.2 Hz; O$_2$C=O), 75.65 (d; J(PC) = 2.9 Hz; C_6H_6), 24.26 (d; J(PC) = 26.4 Hz; PCHCH$_3$), 19.32 (s; PCHCH$_3$). ^{31}P NMR (36.2 MHz, CDCl$_3$): δ 19.85 (s).

3.12. Preparation of [C₆H₆OsCl₂(P'Pr₃)] (16)

150 μl (1.18 mmol) of Me$_3$SiCl was added dropwise to a solution of 142 mg (0.29 mmol) of **15** in 5 ml of CH$_2$Cl$_2$ and stirred for 30 min at room temperature. The solution was concentrated to ca. 2 ml in vacuo and 25 ml of pentane was added. The orange-yellow solid precipitate was characterized spectroscopically by comparison with an authentic sample [6].

3.13. Preparation of [C₆H₆Os(η²-ON= CMe'Bu)(P-'Pr₃)]PF₆ (17)

A suspension of 84 mg (0.17 mmol) of **16** in 5 ml of acetone was treated with 35 mg (0.19 mmol) of KPF$_6$ and 25 mg (0.18 mmol) of Na[ON=CMe^{t}Bu] and the mixture was stirred for 10 min at room temperature. (Note: if the reaction mixture was stirred for a longer period of time, a mixture of **17** and **18b** was isolated.) The solution was worked up as described for **6**. Yellow crystals were isolated. Yield 85 mg (73%); dec. temp. 148°C; $A = 81$ cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 36.39; H, 5.67; N, 1.94. $C_{21}H_{39}F_6NOOsP_2$. Calc.: C, 36.68; H, 5.72; N, 2.04%. ^{1}H NMR (90 MHz, CD$_3$NO$_2$): δ 6.21 (s; 6H; C_6H_6), 2.43 (m; 3H;

PCHCH$_3$), 2.16 (s; 3H; N=CCH$_3$), 1.36 (s; 9H; N=CCCH$_3$), 1.27 and 1.26 (both dd; J(PH) = 14.0, J(HH) = 7.1 Hz; 9H each; PCHCH_3). ^{13}C NMR (22.5 MHz, CD$_3$NO$_2$): δ 152.25 (s; N=C), 79.24 (d; J(PC) = 2.2 Hz; C_6H_6), 38.51 (s; N=CCCH$_3$), 28.14 (s; N=CCCH$_3$), 26.50 (d; J(PC) = 27.1 Hz; PCHCH$_3$), 20.11 (s; PCHCH$_3$), 16.70 (s; N=CCH$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 19.51 (s; P^{i}Pr$_3$), -144.42 (sept; J(PF) = 707.5 Hz; PF$_6$).

3.14. Preparation of [C$_6$H$_6$Os(= N= CMe^{t}Bu)(P^{i}Pr$_3$)]I (18a)

A suspension of 149 mg (0.22 mmol) of **1** in 5 ml of methanol was treated with 40 mg (0.29 mmol) of Na[ON=CMe^{t}Bu] and the mixture was stirred for 45 min at room temperature. The solvent was removed and the residue was worked up as described for **12**. After recrystallization from CH$_2$Cl$_2$–pentane, an orange microcrystalline solid was obtained. Yield 42 mg (29%); dec. temp. 75°C; Λ = 67 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 37.83; H, 5.79; N, 1.96. C$_{21}$H$_{39}$INOsP. Calc.: C, 38.59; H, 6.01; N, 2.14%. ^{1}H NMR (60 MHz, CD$_3$NO$_2$): δ 6.18 (s; 6H; C$_6$H$_6$), 2.68 (d; J(PH) = 1.6 Hz; 3H; N=CCH$_3$), 2.33 (m; 3H; PCHCH$_3$), 1.27 (dd; J(PH) = 14.2, J(HH) = 6.1 Hz; 18H; PCHCH_3), 1.17 (s; 9H; N=CCCH$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 27.15 (s).

3.15. Preparation of [C$_6$H$_6$Os(= N= CMe^{t}Bu)(P^{i}Pr$_3$)]PF$_6$ (18b)

Compound **18b** was prepared as described for **18a** starting from 144 mg (0.21 mmol) of **1**, 45 mg (0.24 mmol) of KPF$_6$ and 40 mg (0.29 mmol) of Na[ON=CMe^{t}Bu]. An orange microcrystalline solid was obtained. Yield 94 mg (67%); dec. temp. 118°C; Λ = 79 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 37.12; H, 5.77; N, 1.91. C$_{21}$H$_{39}$F$_6$NOsP$_2$. Calc.: C, 37.55; H, 5.85; N, 2.09%. ^{1}H NMR (200 MHz, CD$_3$NO$_2$): δ 6.16 (s; 6H; C$_6$H$_6$), 2.69 (d; J(PH) = 1.8 Hz; 3H; N=CCH$_3$), 2.32 (m; 3H; PCHCH$_3$), 1.27 (dd; J(PH) = 14.5, J(HH) = 7.2 Hz; 18H; PCHCH_3), 1.10 (s; 9H; N=CCCH$_3$). ^{13}C NMR (50.3 MHz, CD$_3$NO$_2$): δ 166.13 (d; J(PC) = 3.9 Hz; N=C), 80.21 (d; J(PC) = 2.4 Hz; C_6H_6), 29.30 (s; N=CCCH$_3$), 28.68 (d; J(PC) = 3.0 Hz; N=CCCH$_3$), 27.31 (d, J(PC) = 29.0 Hz; PCHCH$_3$), 21.29 and 20.61 (both s; PCHCH$_3$), 10.56 (d, J(PC) = 3.3 Hz; N=CCH$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 27.19 (s; P^{i}Pr$_3$), -145.51 (sept; J(PF) = 706.4 Hz; PF$_6$).

3.16. Preparation of [C$_6$H$_6$Os(= N= CMe^{t}Bu)(PMe^{t}Bu$_2$)]PF$_6$ (19)

Compound **19** was prepared as described for **18a** starting from 191 mg (0.28 mmol) of **2**, 55 mg (0.30

mmol) of KPF$_6$ and 40 mg (0.29 mmol) of Na[ON=CMe^{t}Bu]. An orange microcrystalline solid was obtained. Yield 77 mg (41%); dec. temp. 122°C; Λ = 82 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 37.29; H, 5.94; N, 1.98. C$_{21}$H$_{39}$F$_6$NOsP$_2$. Calc.: C, 37.55; H, 5.85; N, 2.09%. ^{1}H NMR (60 MHz, CD$_3$NO$_2$): δ6.12 (s; 6H; C$_6$H$_6$), 2.67 (d; J(PH) = 1.8 Hz; 3H; N=CCH$_3$), 1.67 (d; J(PH) = 8.8 Hz; 3H; PCH$_3$), 1.24 (d; J(PH) = 14.2 Hz; 9H; PCCH$_3$), 1.12 (s; 9H; N=CCCH$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 21.93 (s; PMe^{t}Bu$_2$), -144.37 (sept; J(PF) = 707.1 Hz; PF$_6$).

3.17. Preparation of [(mes)Os(= N= CMe^{t}Bu)(P^{i}Pr$_3$)]PF$_6$ (20)

Compound **20** was prepared as described for **12** starting from 141 mg (0.26 mmol) of **3**, 50 mg (0.27 mmol) of KPF$_6$ and 40 mg (0.29 mmol) of Na[ON=CMe^{t}Bu]. An orange microcrystalline solid was obtained. Yield 112 mg (59%); dec. temp. 186°C; Λ = 82 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 39.77; H, 6.43; N, 1.94. C$_{24}$H$_{45}$F$_6$NOsP$_2$. Calc.: C, 40.39; H, 6.35; N, 1.96%. ^{1}H NMR (90 MHz, CD$_3$NO$_2$): δ 5.93 (s; 3H; C$_6$H$_3$Me$_3$), 2.71 (d; J(PH) = 1.8 Hz; 3H; N=CCH$_3$), 2.51 (s; 9H; C$_6$H$_3$Me$_3$), 2.31 (m; 3H; PCHCH$_3$), 1.28 and 1.27 (both dd; J(PH) = 14.0, J(HH) = 7.1 Hz; 9H each; PCHCH_3), 1.11 (s; 9H; N=CCCH$_3$). ^{13}C NMR (22.5 MHz, CD$_3$NO$_2$): δ 165.84 (d; J(PC) = 4.4 Hz; N=C), 95.20 (d; J(PC) = 2.2 Hz; CCH$_3$ of mes), 81.04 (d; J(PC) = 2.9 Hz; CH of mes), 30.16 (d; J(PC) = 2.9 Hz; N=CCCH$_3$), 29.31 (s; N=CCCH$_3$), 27.31 (d, J(PC) = 28.6 Hz; PCHCH$_3$), 20.89 and 20.63 (both s; PCHCH$_3$), 20.01 (s; CCH$_3$ of mes), 11.05 (d, J(PC) = 3.7 Hz; N=CCH$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 26.83 (s; P^{i}Pr$_3$), -144.02 (sept; J(PF) = 707.6 Hz; PF$_6$).

3.18. Preparation of [C$_6$H$_6$Os(= N= CHPh)(P^{i}Pr$_3$)]-PF$_6$ (21)

A solution of 129 mg (0.20 mmol) of **7** in 10 ml of CH$_2$Cl$_2$ was treated with 100 μl (0.67 mmol) of Me$_3$SiN=CHPh and stirred for 12 h at room temperature. The solvent was removed, the residue was washed three times with 10 ml of ether and then dissolved in 1 ml of CH$_2$Cl$_2$. The solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V, 2 cm column) and the orange-red fraction, eluted with CH$_2$Cl$_2$, was worked up as described for **12**. Orange crystals were obtained. Yield 107 mg (79%); dec. temp. 162°C; Λ = 73 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 39.04; H, 5.13; N, 1.93. C$_{22}$H$_{33}$F$_6$NOsP$_2$. Calc.: C, 38.99; H, 4.91; N, 2.07%. ^{1}H NMR (90 MHz, CD$_3$NO$_2$): δ 7.43 (m; 5H; C$_6$H$_5$), 6.27 (s; 6H; C$_6$H$_6$), 2.75 (d; J(PH) = 7.8 Hz; 1H; N=CH), 2.40 (m; 3H; PCHCH$_3$), 1.26 and 1.18 (both dd; J(PH) = 14.6, J(HH) = 7.2 Hz; 9H each;

PCHCH_3). ^{13}C NMR (22.5 MHz, CD$_3$NO$_2$): δ 150.96 (d; J(PC) = 5.1 Hz; N= C), 132.25, 129.58, 129.06 and 121.88 (all s; C$_6$H$_5$), 81.17 (d; J(PC) = 2.9 Hz; C$_6$H$_6$), 26.91 (d; J(PC) = 29.3 Hz; PCHCH$_3$), 20.14 and 19.88 (both s; PCHCH_3). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 30.37 (s; P^{i}Pr$_3$), −144.37 (sept; J(PF) = 707.1 Hz; PF$_6$).

3.19. Preparation of [C$_6$H$_6$Os(= N= CEtPh)(P^{i}Pr$_3$)]-PF$_6$ (22)

A solution of 187 mg (0.29 mmol) of 7 in 10 ml of CH$_2$Cl$_2$ was treated with 100 μl (0.83 mmol) of HN=CEtPh. After the solution had been stirred for 1 h at room temperature, it was concentrated to ca. 3 ml in vacuo and 25 ml of ether was added. The orange solid precipitate was filtered, washed twice with 5 ml of ether and dried. Yield 167 mg (82%); dec. temp. 124°C; Λ = 78 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 40.90; H, 5.53; N, 1.88. C$_{24}$H$_{37}$F$_6$NOsP$_2$. Calc.: C, 40.80; H, 5.28; N, 1.98%. ^{1}H NMR (200 MHz, CD$_3$NO$_2$): δ 7.47 and 7.31 (both m; 5H; C$_6$H$_5$), 6.32 (s; 6H; C$_6$H$_6$), 3.51 (ddq; J(PH) = 1.8, J(HH) = 16.1 and 7.5 Hz; 1H of CH_2CH$_3$), 3.15 (ddq; J(PH) = 1.4, J(HH) = 16.1 and 7.5 Hz; 1H of CH_2CH$_3$), 2.30 (m; 3H; PCHCH$_3$), 1.22 and 1.06 (both dd; J(PH) = 14.6, J(HH) = 7.2 Hz; 9H each; PCHCH_3), 1.15 (t; J(HH) = 7.5 Hz; 3H; CH$_2$CH_3). ^{13}C NMR (50.3 MHz, CD$_3$NO$_2$): δ 159.63 (d; J(PC) = 4.6 Hz; N= C), 131.20, 129.26, and 128.88 (all s; ortho-, meta-, para-C of C$_6$H$_5$), 123.38 (d; J(PC) = 3.5 Hz; ipso-C of C$_6$H$_5$), 80.74 (s; C$_6$H$_6$), 26.85 (d; J(PC) = 29.2 Hz; PCHCH$_3$), 20.16 and 19.95 (both s; PCHCH_3), 18.20 (d; J(PC) = 2.7 Hz; CH_2CH$_3$), 13.17 (s; CH$_2$CH_3). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 30.72 (s; P^{i}Pr$_3$), −144.42 (sept; J(PF) = 706.6 Hz; PF$_6$).

3.20. Preparation of [C$_6$H$_6$Os(= N= CMe$_2$)(P^{i}Pr$_3$)]-PF$_6$ (23)

A solution of 137 mg (0.21 mmol) of 7 in 5 ml of CH$_2$Cl$_2$ was treated with 100 μl (0.92 mmol) of HN=CMe(OEt). After the solution had been stirred for 15 h at room temperature, it was concentrated to ca. 1 ml in vacuo and then chromatographed on Al$_2$O$_3$ (neutral, activity grade V, 5 cm column). The orange-red fraction eluted with CH$_2$Cl$_2$, was worked up as described for 12. Orange crystals were obtained. Yield 47 mg (36%); dec. temp. 169°C; Λ = 71 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 34.22; H, 4.78; N, 2.06. C$_{18}$H$_{33}$F$_6$NOsP$_2$. Calc.: C, 34.34; H, 5.28; N, 2.22%. ^{1}H NMR (60 MHz, CD$_3$NO$_2$): δ 6.03 (s; 6H; C$_6$H$_6$), 2.68 (d; J(PH) = 1.8 Hz; 6H; N=CCH_3), 2.38 (m; 3H; PCHCH$_3$), 1.25 (dd; J(PH) = 14.3, J(HH) = 6.5 Hz; 18H; PCHCH_3). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ

29.89 (s; P^{i}Pr$_3$), −145.48 (sept; J(PF) = 706.9 Hz; PF$_6$).

3.21. Preparation of [(mes)Os(= N= CEtPh)(P^{i}Pr$_3$)]-PF$_6$ (24)

Compound 24 was prepared as described for 22 starting from 75 mg (0.11 mmol) of 10 and 100 μl (0.83 mmol) of HN=CEtPh. An orange microcrystalline solid was obtained. Yield 78 mg (95%); dec. temp. 124°C; Λ = 80 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 43.31; H, 5.97; N, 1.76. C$_{27}$H$_{43}$F$_6$NOsP$_2$. Calc.: C, 43.37; H, 5.80; N, 1.87%. ^{1}H NMR (200 MHz, CD$_3$NO$_2$): δ 7.51 and 7.29 (both m; 5H; C$_6$H$_5$), 6.11 (s; 3H; C$_6$H$_3$Me$_3$), 3.32 (dq; J(PH) = 1.4, J(HH) = 7.5 Hz; 2H; CH_2CH$_3$), 2.60 (s; 9H; C$_6$H$_3$Me$_3$), 2.25 (m; 3H; PCHCH$_3$), 1.25 and 1.09 (both dd; J(PH) = 14.4, J(HH) = 7.2 Hz; 9H each; PCHCH_3), 1.17 (t; J(HH) = 7.5 Hz; 3H; CH$_2$CH_3). ^{13}C NMR (50.3 MHz, CD$_3$NO$_2$): δ 160.10 (d; J(PC) = 3.1 Hz; N= C), 131.24, 129.41, and 128.72 (all s; ortho-, meta-, and para-C of C$_6$H$_5$), 123.96 (d; J(PC) = 3.0 Hz; ipso-C of C$_6$H$_5$), 95.55 (s; CCH$_3$ of mes), 81.94 (s; CH of mes), 27.25 (d; J(PC) = 28.8 Hz; PCHCH$_3$), 20.74 (s; CCH$_3$ of mes), 20.38 and 19.99 (both s; PCHCH_3), 19.62 (d; J(PC) = 2.5 Hz; CH_2CH$_3$), 14.00 (s; CH$_2$CH_3). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 28.40 (s; P^{i}Pr$_3$), −144.68 (sept; J(PF) = 707.1 Hz; PF$_6$).

3.22. Preparation of [(mes)Os(= N= CPh$_2$)(PMe^{t}Bu$_2$)]PF$_6$ (25)

A solution of 145 mg (0.21 mmol) of 14 in 10 ml of CH$_2$Cl$_2$ was treated with 100 μl (0.58 mmol) of HN=CPh$_2$ and stirred for 30 min at room temperature. The solution was concentrated to ca. 1 ml in vacuo and 10 ml of Et$_2$O was added. The precipitated orange-red crystals were filtered, washed three times with 10 ml pentane, and dried. Yield 145 mg (87%); dec. temp. 187°C; Λ = 67 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C, 47.01; H, 5.62; N, 1.69. C$_{31}$H$_{43}$F$_6$NOsP$_2$. Calc.: C, 46.78; H, 5.45; N, 1.76%. ^{1}H NMR (90 MHz, CD$_3$NO$_2$): δ 7.50 (m; 10H; C$_6$H$_5$), 6.28 (s; 3H; C$_6$H$_3$Me$_3$), 2.51 (s; 9H; C$_6$H$_3$Me$_3$), 1.95 (d; J(PH) = 8.7 Hz; 3H; PCH$_3$), 1.09 (d; J(PH) = 14.3 Hz; 18H; PCCH$_3$). ^{31}P NMR (36.2 MHz, CD$_3$NO$_2$): δ 19.99 (s; PMe^{t}Bu$_2$), −145.10 (sept; J(PF) = 706.5 Hz; PF$_6$).

3.23. Preparation of [(mes)Os(= N= CEtPh)(PMe^{t}Bu$_2$)]PF$_6$ (26)

Compound 26 was prepared as described for 25 starting from 145 mg (0.21 mmol) of 14 and 70 μl (0.58 mmol) of HN=CEtPh. An orange microcrystalline solid was obtained. Yield 128 mg (82%); dec. temp. 184°C; Λ = 74 cm^2 Ω^{-1} mol^{-1}. Anal. Found: C,

43.31; H, 5.69; N, 2.05. $C_{27}H_{43}F_6NOsP_2$. Calc.: C, 43.37; H, 5.80; N, 1.87%. ^1H NMR (90 MHz, CD_3NO_2): δ 7.40 (m; 5H; C_6H_5), 6.24 (s; 3H; $C_6H_3Me_3$), 3.50 and 3.41 (both ddq; J(PH) = 1.4, J(HH) = 14.8 and 7.4 Hz; 1H each; CH_2CH_3), 2.50 (s; 9H; $C_6H_3Me_3$), 1.96 (d; J(PH) = 8.5 Hz; 3H; PCH_3), 1.19 (t; J(HH) = 7.4 Hz; 3H; CH_2CH_3), 1.23 and 0.99 (both d; J(PH) = 14.2 Hz; 9H each; $PCCH_3$). ^{13}C NMR (50.3 MHz, CD_3NO_2): δ 160.48 (d; J(PC) = 3.8 Hz; $N=C$), 131.29, 129.42, and 128.53 (all s; ortho-, meta-, and para-C of C_6H_5), 123.51 (d; J(PC) = 3.9 Hz; ipso-C of C_6H_5), 93.28 (d; J(PC) = 2.0 Hz; CCH_3 of mes), 83.70 (d; J(PC) = 1.7 Hz; CH of mes), 37.16 and 36.80 (both d; J(PC) = 24.5 Hz; $PCCH_3$), 29.96 and 29.73 (both d; J(PC) = 4.0 Hz; $PCCH_3$), 20.09 (s; CCH_3 of mes), 19.21 (d; J(PC) = 2.7 Hz; CH_2CH_3), 13.92 (s; CH_2CH_3), 12.35 (d; J(PC) = 32.2 Hz; PCH_3). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ 18.05 (s; PMe^tBu_2), -144.96 (sept; J(PF) = 707.2 Hz; PF_6).

3.24. Crystal structure analysis of 18b

Single crystals were grown by slow diffusion of pentane into a solution of 18b in CH_2Cl_2. Crystal data (from 24 reflections with $11° < \Theta < 14°$): monoclinic space group $P2_1/c$ (No.14), $a = 13.32(1)$ Å, $b = 39.08(1)$ Å, $c = 15.63(1)$ Å, $\beta = 101.81(5)°$, $V = 7971$ Å^3, $Z = 12$, $d_{calcd} = 1.782$ g cm^{-3}, $\mu(Mo\,K\alpha) = 51.6$ cm^{-1}. Crystal size 0.4 × 0.2 × 0.15 mm^3. Enraf Nonius CAD4 diffractometer, Mo $K\alpha$ radiation (0.70930 Å), graphite monochromator, $T = 293$ K, $\omega/2\Theta$ scan, max. $2\Theta = 40°$; 7982 reflections were measured, 7563 were independent, and 4654 were regarded as being observed $[F_o > 3\sigma(F_o)]$; intensity data were corrected for Lorentz and polarization effects, empirical absorption correction (Ψ-scan method) was applied, minimum transmission was 84.48%. The structure was solved by direct methods; atomic coordinates were refined by full-matrix least squares (673 parameters, unit weights, Enraf–Nonius SDP) [14]. There are three independent molecules in the unit cell, of which the first (molecule 1) was designated as Os, Cl etc., the second (molecule 2) as Os*, Cl* etc., and the third (molecule 3) as Os**, Cl** etc. From molecules 1 and 2 all non-hydrogen atoms with the exception of the phenyl carbon atoms were refined anisotropically; from molecule 3 only the Os, N, P and F atoms were refined anisotropically (owing to the high number of parameters). The hydrogen atoms were placed in calculated positions (distance C–H 0.95 Å) and, for molecules 1 and 2, were considered only for the calculation of F_c. $R = 0.045$, $R_w = 0.051$; reflex/parameter ratio 6.9; residual electron

density $+1.02/-0.88$ e Å^{-3}. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-59039, the names of the authors, and the journal citation.

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