Articles

(Arene)osmium Complexes Containing Alkynyl, Vinyl, Vinylidene, and Thio- and Selenoketene Units as Ligands: A Series of Organometallic Compounds Built Up from 1-Alkynes[1]

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The reaction of $[(C_6H_6)Os(PR'_3)I_2]$ (**1**, **2**) with $AgPF_6$ and 1-alkynes gives the osmium alkynyls $[(C_6H_6)Os(C{\equiv}CR)(PR'_3)I]$ (**3–9**), which on treatment with $NaBH_4$ in methanol or ethanol afford the hydrido vinyl complexes $[(C_6H_6)OsH(CH{=}CHR)(PR'_3)]$ (**10–16**) in good to excellent yields. Further experiments prove that the hydride ligand in these compounds is generated from the alkoxide ion. Complexes **10–16**, in the presence of CCl_4, $CHBr_3$, and CH_2I_2, undergo metathesis to give the halogenovinylosmium derivatives $[(C_6H_6)Os(CH{=}CHR)(PR'_3)X]$ (**17–26**). The trans configuration at the vinylic carbon–carbon double bond has been confirmed by NMR spectroscopy as well as by a single-crystal X-ray investigation of $[(C_6H_6)Os(CH{=}CHPh)(P^iPr_3)I]$ (**21**). Compound **21** crystallizes in the space group $C2/c$ with a = 23.323 (6) Å, b = 15.697 (7) Å, c = 15.832 (5) Å, and β = 117.42 (2)°. The osmium atom is surrounded by the four ligands in a quasi-octahedral configuration with a planar benzene ring and bond angles I–Os–P, I–Os–C, and P–Os–C of 85–92°. The halogeno vinyl complexes **19–21**, **23**, **25**, and **26** react with *tert*-butyllithium at low temperature to form the osmium(0) vinylidenes $[(C_6H_6)Os(=C{=}CHR)(PR'_3)]$ (**30–33**). The reactivity of these "metallaallenes" is governed by the nucleophilicity of the Os=C bond. Therefore, on addition of electrophiles such as HX (X = Cl, CF_3CO_2), iodine, sulfur, and selenium the corresponding vinyl, thioketene, and selenoketene complexes **19**, **22–26**, **35**, and **37–43** are obtained. The reaction of **30–32** with CuCl affords the heterometallic vinylidene-bridged compounds $[(C_6H_6)(PR'_3)Os(\mu\text{-}C{=}CHR)CuCl]_n$ (**44–46**), which on treatment with NaC_5H_5 or LiC_5Me_5 give the cyclopentadienyl and pentamethylcyclopentadienyl derivatives $[(C_6H_6)(PR'_3)Os(\mu\text{-}C{=}CHR)Cu(C_5R_5)]$ (**47–49**). From **30** and benzoyl azide, the *E* and *Z* isomers of the five-membered metallaheterocycle $[(C_6H_6)(P^iPr_3)OsC(=CHPh)NC(Ph)O]$ (**50**) are prepared.

Introduction

The chemistry of vinylidene transition-metal complexes has become increasingly attractive in recent years.[2] Mononuclear compounds of the general type $[L_nM{=}C{=}CRR']$ have mainly been prepared by two routes either from alkynes, which are converted in the coordination sphere of the metal into the isomeric vinylidenes, or from alkynylmetal derivatives, which upon addition of an electrophile (usually a proton or an alkylcarbenium cation) to the β-carbon atom of the M–C≡C–R unit are transformed into the target molecule.[2]

Following our work on alkyne- and vinylidene-containing rhodium and iridium complexes,[3] we have recently shown that *cationic* osmium vinylidene compounds $[(arene)Os(=C{=}CHR)(PR'_3)X]^+$ (with BF_4 or PF_6 as anion) can be obtained on both of the above-mentioned pathways, i.e., directly from $[(arene)Os(PR'_3)X_2]$ (X = Cl, I), $AgPF_6$, and 1-alkynes or from the alkynyls $[(arene)Os(C{\equiv}CR)(PR'_3)X]$ on treatment with an electrophile.[4] We were unable, however, to reduce the cations $[(arene)Os(=C{=}CHR)(PR'_3)X]^+$ to the corresponding neutral complexes $[(arene)Os(=C{=}CHR)(PR'_3)]$ and therefore had to find another route to prepare the osmium(0) vinylidenes.

In the present paper we report on the synthesis of osmium(0) vinylidene half-sandwich type complexes with $(C_6H_6)Os(P^iPr_3)$ and $(C_6H_6)Os(PMe^tBu_2)$ as building blocks and illustrate their potential as starting materials for the preparation of a variety of organometallic osmium derivatives. The key to success to obtain the compounds $[(C_6H_6)Os(=C{=}CHR)(PR'_3)]$ was the elimination of HX from vinylosmium(II) precursors, a method which may become useful also in other instances. A short communication describing some preliminary results of this work has already appeared.[5]

Results

Preparation of Alkynyl- and Vinylosmium(II) Complexes. The route to prepare the osmium alkynyls

(1) Part 18 of the series Vinylidene Transition-Metal Complexes. For part 17, see: Werner, H.; Dirnberger, T.; Höhn, A. *Chem. Ber.* **1991**, *124*, 1957.

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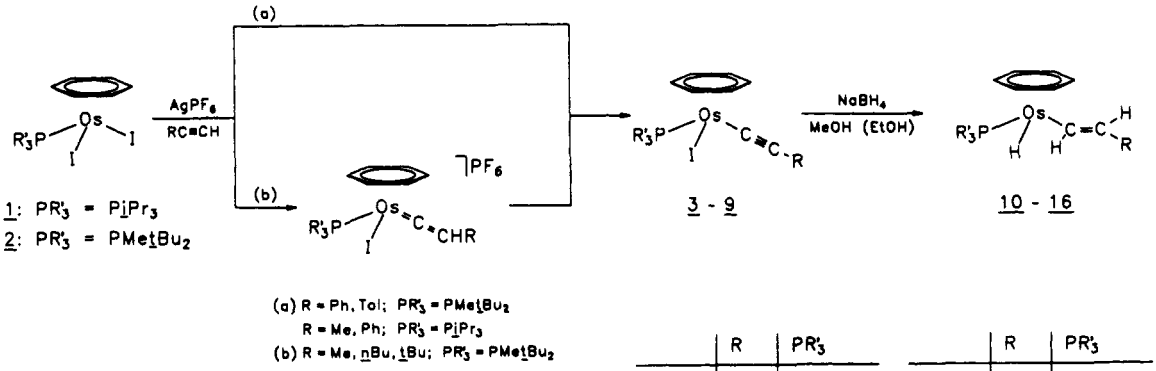
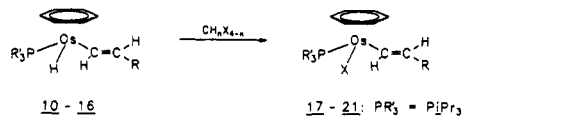
Scheme I



	R	PR'3		R	PR'3
3, 10	Me	PiPr3	7, 14	tBu	PMetBu2
4, 11	Ph	PiPr3	8, 15	Ph	PMetBu2
5, 12	Me	PMetBu2	9, 16	Tol	PMetBu2
6, 13	nBu	PMetBu2			

Scheme II



	X	R		R
17	Cl	Me	22	Me
18	I	Me	23	nBu
19	Cl	Ph	24	tBu
20	Br	Ph	25	Ph
21	I	Ph	26	Tol

3–9, which are used as starting materials for the synthesis of the vinylidene complexes, is outlined in Scheme I. The displacement of one halide ligand in **1** and **2** by the alkynyl anion upon treatment with $AgPF_6$ and the 1-alkyne uses a procedure which has originally been described by Reger[6] and Riera[7] for the preparation of alkynyliron and -manganese compounds. It is interesting to note that *under the same conditions* complex **2**, in the presence of $AgPF_6$, reacts with MeC≡CH, ^{n}BuC≡CH, and ^{t}BuC≡CH to afford the cationic vinylidenes $[(C_6H_6)Os(=C=CHR)(PMe^tBu_2)I]PF_6$ but with PhC≡CH and TolC≡CH to give the neutral alkynyls **8** and **9**.[4] In contrast, the reaction of **1** with $AgPF_6$ and PhC≡CH or MeC≡CH only leads to the formation of the alkynyl complexes **3** and **4**. It is worth mentioning that compound **4** has also been prepared from **1** and AgC≡CPh.

The reaction of the osmium alkynyls **3–9** with $NaBH_4$ does not give, as was originally expected, the alkynylhydridometal compounds $[(C_6H_6)OsH(C{\equiv}CR)(PR'_3)]$ but instead leads to the hydrido vinyl derivatives **10–16** (Scheme I). Although complexes of the general type $L_nMH(CH{=}CHR)$ are well-known and have been prepared with electron-poor[8] as well as electron-rich[9] transition metals, as far as we know there is no precedent for their formation from an alkynylhalogenometal precursor and a hydride source. We note that on treatment of **3–9** with $LiAlH_4$ or $NaBH_4$ in ether, THF, or benzene mainly decomposition occurs whereas with $NaBH_4$ in ethanol or methanol the hydrido vinyl complexes can be isolated in 65–95% yield.

Compounds **10–16**, which, with the exception of **10**, are yellow air-sensitive solids, exhibit remarkable thermal stability and do not react on warming for several hours at 80 °C to form the metal olefin isomers.[10] Such stability is in partial contrast to that of the corresponding carbonyl compounds $[(C_6H_6)OsH(CH{=}CHR)(CO)]$ (R = H, Me), which under similar conditions slowly rearrange to give the alkene complexes $[(C_6H_6)Os(CH_2{=}CHR)(CO)]$.[11]

Evidence for the stereochemistry of the OsCH=CHR unit as shown in Scheme I is mainly supplied by the ^{1}H NMR data (for details see Experimental Section). In particular, the large coupling constant (15.6–16.6 Hz) for the two CH protons confirm the *E* configuration. The assignment of the signal with the lowest chemical shift (δ 7.7–9.3) to the vinylic proton at the α-carbon atom is in full agreement with previous studies by Shaw et al. on a series of vinylplatinum complexes.[12] It is worth mentioning that for **10–16** this signal is not only split by coupling to phosphorus and the vinylic protons on β-C but also by coupling to the metal-bound hydride. An adjacent position of these two protons is therefore inferred.

As far as the mechanism of formation of the hydrido vinyl compounds **10–16** is concerned, we note that ethanol or methanol as solvents are really essential. We therefore assume that the initial step of the reaction is a nucleophilic substitution of iodide by alkoxide followed by a β-hydride shift and elimination of CH_3CHO or CH_2O. Parallel or subsequently, an attack of the hydride donor on the α-carbon atom of the alkynyl ligand takes place leading to the formation of a metal-substituted vinyl carbanion. Final addition of a proton (from the alcohol) produces the OsCH=CHR unit.

The generation of the hydride ligand in the hydrido vinyl complexes from the alkoxide ion has been proved by the formation of **11** from **4** and NaOMe in methanol. The

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(10) For the synthesis of $[(C_6H_6)Os(CH_2{=}CHR)(PMe_3)]$, see: Werner, R.; Werner, H. *Chem. Ber.* **1983**, *116*, 2074.
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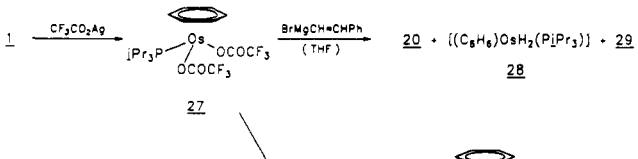
Scheme III



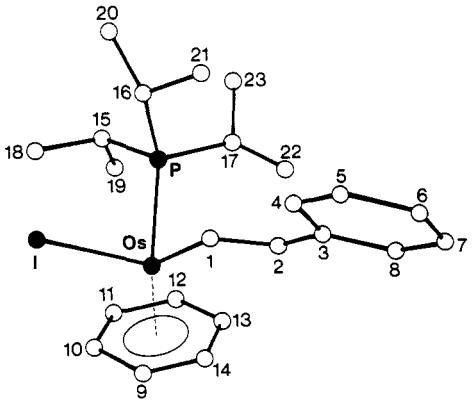


Figure 1. Molecular structure and labeling scheme for **21**.

reaction proceeds at 60 °C and after 16 h gives compound **11** in 63% yield. An almost quantitative yield of **11** is obtained on treatment of the chloro vinyl complex **19** with NaOMe in methanol. This reaction is significantly faster than that of **4** with NaOMe/MeOH, which indicates that the substitution of metal-bound halide by OMe^- is the rate-determining step. The deuterated derivative $[(C_6H_6)OsD(CD{=}CDPh)(P^iPr_3)]$ (**11**-d_3) is formed from **4** and $NaOCD_3$ in CD_3OD.

The hydrido vinyl complexes **10–16**, in the presence of CCl_4, $CHBr_3$, and CH_2I_2, undergo metathesis to give the halogeno vinyl compounds **17–26** (Scheme II). The yield is 80–95%. The reactivity of the halomethanes increases in the order $CH_2I_2 < CHBr_3 < CCl_4$, which corresponds to results obtained by other groups.[13] We note that in the reactions of **10–13**, **15**, and **16** with CH_nX_{4-n} the stereochemistry at the vinyl C=C bond does not change whereas from **14** and CCl_4 a mixture of *E* and *Z* isomers is obtained. At −20 °C, the *E*:*Z* ratio is ca. 3:1. After dissolution of the mixture in nitromethane or acetone and warming of the solution to 50 °C, a complete rearrangement of the *Z* into the thermodynamically more stable *E* isomer occurs. As polar solvents obviously facilitate the isomerization, we assume that a short-lived ionic intermediate $[(C_6H_6)Os(CH{=}CH^tBu)(PMe^tBu_2)]^+$ is involved. A similar rearrangement process has been observed with the vinylrhodium complex $[(C_5H_5)Rh(CH{=}CHPh)(P^iPr_3)O_2CCF_3]$, which is formed on protonation of the corresponding vinylidene derivative with CF_3CO_2H.[14]

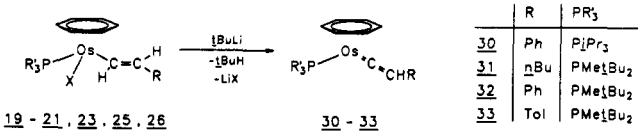
An attempt to prepare the bromo vinyl compound **20** by an independent route has been only partly successful. The reaction of the bis(trifluoroacetate) **27**, which has been obtained from the diiodide **1** and CF_3CO_2Ag, with styrylmagnesium bromide gives a mixture of three compounds **20**, **28**, and **29** (Scheme III) from which the dibromide was separated by column chromatography. It has been prepared in virtually quantitative yield by metathetical reaction of **27** and KBr. The small amounts of the well-known dihydrido complex[15] could not be completely separated from the bromo vinyl compound, indicating that this method is not to be recommended for the synthesis of **20**.

Table I. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations[a] for 21

Bond Distances			
Os–I	2.755 (1)	Os–P	2.372 (2)
Os–C1	2.090 (7)	Os–C9	2.227 (10)
Os–C10	2.221 (12)	Os–C11	2.284 (11)
Os–C12	2.199 (9)	Os–C13	2.188 (13)
Os–C14	2.192 (9)	C1–C2	1.313 (10)
C2–C3	1.478 (9)	P–C15	1.840 (9)
P–C16	1.850 (14)	P–C17	1.836 (18)
Bond Angles			
I–Os–P	92.1 (1)	I–Os–C1	85.3 (2)
P–Os–C1	86.2 (2)	Os–C1–C2	130.5 (6)
C1–C2–C3	127.6 (7)	Os–P–C15	115.3 (3)
Os–P–C16	115.7 (3)	Os–P–C17	114.6 (4)
C15–P–C16	101.0 (4)	C15–P–C17	101.5 (5)
C16–P–C17	106.8 (7)		

[a] Average deviation of the carbon atoms C9–C14 from the best plane of the benzene ring is 0.013 Å.

Scheme IV



	R	PR'_3
30	Ph	P^iPr_3
31	nBu	PMe^tBu_2
32	Ph	PMe^tBu_2
33	Tol	PMe^tBu_2

19 - **21**, **23**, **25**, **26** — **30** - **33**

Molecular Structure of Complex 21. The X-ray structural analysis of the iodo vinyl complex confirms that the two substituents at the C=C double bond are in trans position to each other. As Figure 1 illustrates, the molecule has a quasi-octahedral configuration with a planar benzene ring and bond angles I–Os–P, I–Os–C1, and P–Os–C1 of 85–92°. The plane of the metal, the vinylic carbon atoms C1 and C2, and C3 is nearly perpendicular to the plane formed by Os, I, and P, which owing to MO calculations[16] should be the preferred conformation for vinyl complexes of this structural type. The Os–C1 distance (2.09 Å) (Table I) is significantly longer than in the five-coordinate chlorovinylosmium compound $[Os(E\text{-}CH{=}CHPh)Cl(CO)(P^iPr_3)_2]$ (1.99 Å)[17] but comparable to the Os–C(C_6H_5) bond lengths in the carbene complex $\{(1,3,5\text{-}C_6H_3Me_3)Os[{=}C(NHMe)Ph](C_6H_5)_2\}$ (2.09 and 2.10 Å).[18] The other metal-to-ligand distances Os–I, Os–P, and Os–C(ring) are comparable to those of related (arene)osmium phosphine compounds[18-21] and need no further comment.

Synthesis of Osmium(0) Vinylidenes. The crucial step in the synthesis of the formerly unknown osmium(0) vinylidenes $[(C_6H_6)Os(=C{=}CHR)(PR'_3)]$ is the elimination of HX from the halogeno vinyl complexes $[(C_6H_6)Os(CH{=}CHR)(PR'_3)X]$. In contrast to the related rhodium compound $[(C_5H_5)Rh(CH{=}CHPh)(P^iPr_3)OC(O)CF_3]$,[14] the osmium derivatives **19–21**, **23**, **25**, and **26** are completely inert toward NEt_3 and even to $NaNH_2$. They

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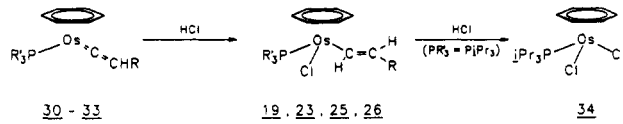
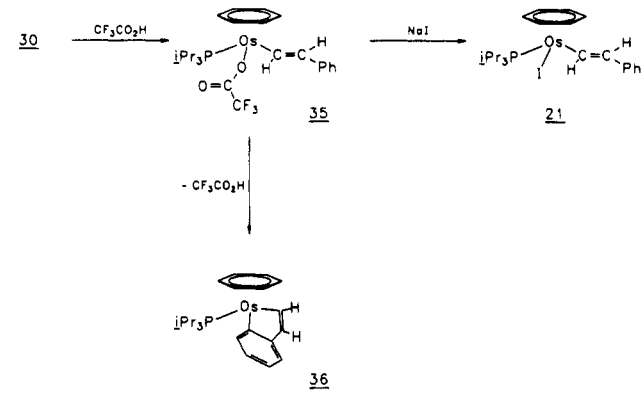
Scheme V



30 - 33 19, 23, 25, 26 34

Scheme VI



35 21 36

react, however, with ^{t}BuLi in ether at low temperature to produce the vinylidene complexes **30–33** (Scheme IV). The elimination process is accompanied by a characteristic color change from yellow to deep violet, which turns to yellow again as long as no excess of ^{t}BuLi is present. The violet species could possibly be a lithiated compound containing either a Os—C(Li)=CHR or Os=C=C(Li)R unit. After destruction of the excess of *tert*-butyllithium with methanol at −78 °C, removal of the solvent, and chromatographic workup using basic Al_2O_3, yellow-brown crystalline solids are obtained. They have been characterized by MS and elemental analysis. On treatment of the propenyl compounds **17** and **22** with ^{t}BuLi, probably also osmium(0) vinylidenes $[(C_6H_6)Os(=C=CHMe)(PR'_3)]$ are formed, but despite several attempts, they could not be isolated in analytically pure form. We note that, also in the rhodium series, the methyl-substituted complex $[(C_5H_5)Rh(=C=CHMe)(P^iPr_3)]$ is more labile than the phenylvinylidene derivative.[3d]

The most interesting feature of the spectroscopic data of compounds **30–33** is the position of the signal of the vinylidene α-C atom in the ^{13}C NMR spectra, which appears at ca. δ 278 ppm showing a strong P–C coupling of 21–22 Hz. In the related cyclopentadienylrhodium complexes $[(C_5H_5)Rh(=C=CHR)(P^iPr_3)]$[3d,f] and also in the vinylideneosmium cations $[(C_6H_6)Os(=C=CHR)(PR'_3)X]^+$,[4] the α-C resonance is found even at lower field (δ 300–310 ppm). In the ^{1}H NMR spectra of **31–33**, two signals for the protons of the phosphine *tert*-butyl groups are observed, which is in full agreement with the allene-type structure of the osmium(0) vinylidenes.

Electrophilic Addition Reactions of Complexes 30–33. In analogy to the cyclopentadienylrhodium vinylidenes $[(C_5H_5)Rh(=C=CHR)(P^iPr_3)]$,[14,22-24] the chemistry of the related (benzene)osmium derivatives **30–33** is also governed by the tendency to add electrophiles at the Os=C bond. With an equimolar amount of HCl (in benzene), the chloro vinyl complexes **19**, **23**, **25**, and **26** are formed (Scheme V), which—as mentioned above—are also obtained from the hydrido vinyl compounds **11**, **13**, **15**, and **16** and CCl_4. Similarly, the reaction of **30** with CF_3CO_2H leads to the formation of the vinyl trifluoroacetate **35**, which on metathesis with NaI gives the iodo complex **21**. Treatment of **30** with excess HCl yields the dichloro compound **34**, which represents another member of the $[(C_6H_6)OsX_2(P^iPr_3)]$ series.

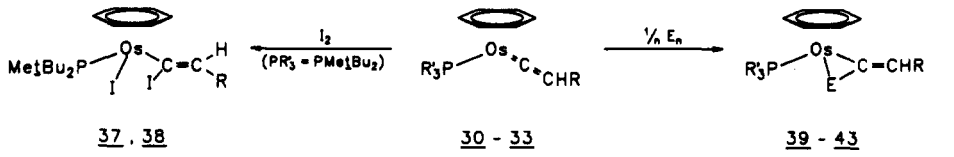
In contrast to the complexes **19** and **22–26**, the vinyl trifluoroacetate **35** is relatively labile and reacts already at room temperature (in methanol) to form the metallacycle **36** (Scheme VI). It is interesting to note that the smooth elimination of CF_3CO_2H does not regenerate the vinylidene compound **30** (which was used for the preparation of **35**) but instead leads to the cyclic isomer. The proposed structure is mainly supported by the ^{1}H NMR spectrum, which shows two doublets of doublets for the Os—C*H*=C*H*C_6H_4 olefinic protons at fairly low field. Related metallacycles with a five-membered M—2-C_6H_4CH=CPh ring (M = Rh, Ir) have recently been described and were prepared from the vinyl complexes $[(C_5H_5)M(CPh=CHPh)(P^iPr_3)(O_2CCF_3)]$ by CF_3CO_2H elimination.[25,26]

A similar reaction as was observed with HX also takes place between the osmium(0) vinylidenes and I_2. On treatment of ether solutions of the compounds **32** and **33** with an equimolar amount of iodine, almost immediately (even at −78 °C) the precipitation of yellow solids is observed, which owing to elemental analyses and spectroscopic data are the iodo vinyl complexes **37** and **38** (Scheme VII). They are formed like the analogues **23** and **25** by addition of the electrophile to the Os=C bond. If solutions of **37** and **38** in dichloromethane are chromatographed on deactivated alumina, a smooth elimination of HI occurs and the osmium alkynyls **8** and **9** are obtained. Concerning the structure of **37** and **38**, we assume according to the chemical shift of the vinylic proton an *E* configuration, as shown in Scheme VII. It is worth mentioning that there is no indication for cleavage of the Os=C bond in **32** and **33** by iodine as was observed in case of analogous metal carbene complexes.[27]

Compounds **30–32** also react with sulfur and (red) selenium to give the intensely colored osmium thio- and selenoketene complexes **39–43** (Scheme VII). These reactions are significantly slower than those of the rhodium compounds $[(C_5H_5)Rh(=C=CHR)(P^iPr_3)]$ with the chalcogens, which is consistent with the frequently observed lower reactivity of 5d metal compounds compared with their 4d analogues. We note that free thioketenes are extremely reactive molecules and can only be isolated if the β-carbon atom bears bulky or strongly electron-withdrawing substituents.[28] Selenoketenes Se=C=CRR', where R and R' is alkyl or aryl, are unknown.[28b] As in the ^{1}H and ^{31}P NMR spectra of **39–43** only one set of signals is observed, we assume that the addition of sulfur or selenium leads stereoselectively to one diastereomer. If the kinetically preferred product is formed, the attack of the chalcogen probably occurs at that side of the C=C bond in the osmium(0) vinylidenes which is less shielded and, therefore, the *Z* isomer should be obtained. In case of the rhodium compounds $[(C_5H_5)Rh(\eta^2\text{-}E=C=CHR)(P^iPr_3)]$,

(22) Wolf, J.; Zolk, R.; Schubert, U.; Werner, H. *J. Organomet. Chem.* **1988**, *340*, 161.
(23) Werner, H.; Wolf, J.; Müller, G.; Krüger, C. *J. Organomet. Chem.* **1988**, *342*, 381.
(24) Werner, H.; Garcia Alonso, F. J.; Otto, H.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1988**, *121*, 1565.
(25) Werner, H.; Wolf, J.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* **1986**, *317*, 327.
(26) Werner, H.; Höhn, A. *J. Organomet. Chem.* **1984**, *272*, 105.
(27) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983.
(28) (a) Bock, H.; Aygen, S.; Rosmus, P.; Solouki, B. *Chem. Ber.* **1980**, *113*, 3187. (b) Hogg, D. R.; Lundquist, J. K.; Ohno, A. *Org. Comp. Sulfur, Selenium, Tellurium* **1981**, *6*, 131. (c) Harrit, N.; Rosenkilde, S.; Larsen, B. D.; Holm, A. *J. Chem. Soc., Perkin Trans. 1*, **1985**, 907.

Scheme VII

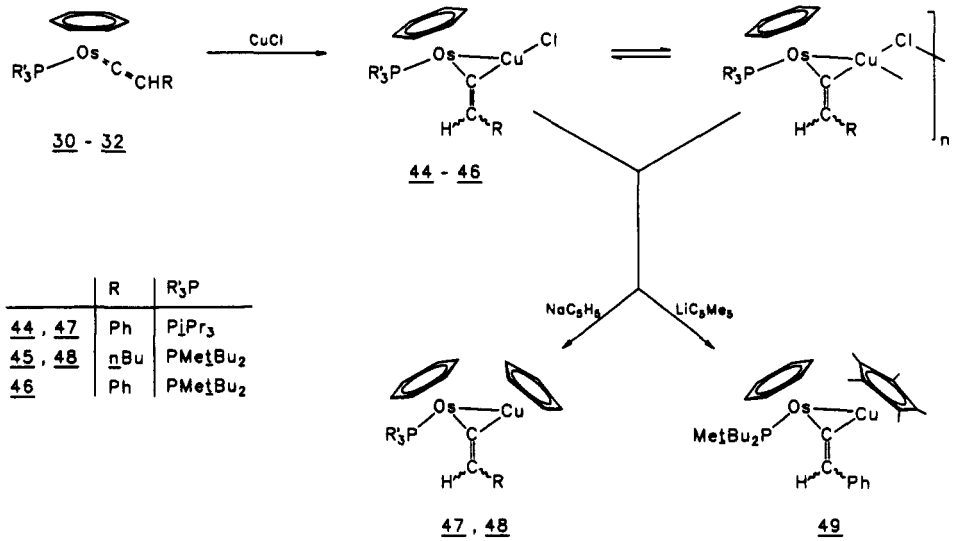


37, 38 30 - 33 39 - 43

	R
37	Ph
38	Tol

	E	R	PR'_3
39	S	Ph	$PiPr_3$
40	Se	Ph	$PiPr_3$
41	S	nBu	$PMetBu_2$
42	Se	nBu	$PMetBu_2$
43	Se	Ph	$PMetBu_2$

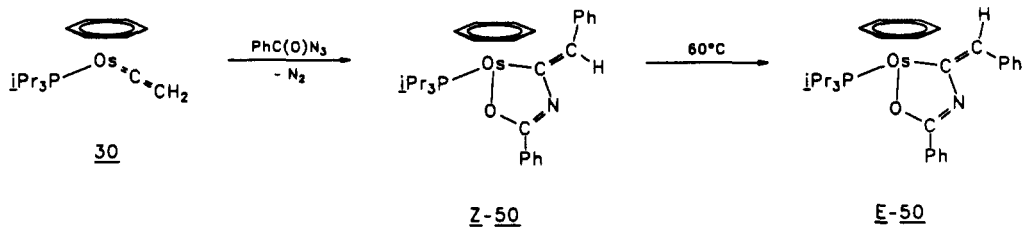
Scheme VIII



30 - 32 44 - 46 47, 48 49

	R	R'_3P
44, 47	Ph	$PiPr_3$
45, 48	nBu	$PMetBu_2$
46	Ph	$PMetBu_2$

Scheme IX



30 Z-50 E-50

the NMR data have been interpreted as being in support of this proposal.[22]

The reaction of **30–32** with CuCl affords the heterometallic dinuclear complexes **44–46** in which only the α-carbon atom of the vinylidene unit bridges the two metal atoms. Depending on the conditions under which the compounds **45** and **46** are precipitated from solution, either a yellow or an orange-red solid has been isolated. As these substances differ significantly in their solubility, e.g., in CH_2Cl_2 or THF, we assume that besides a monomeric also a dimeric or possibly polymeric form exists. A similar situation has previously been observed for $[(C_5H_5)(P^iPr_3)Rh(\mu\text{-}C{=}CH_2)CuCl]$.[23] The ^1H NMR spectra of the monomeric form of **44–46** leave no doubt that in each case only one stereoisomer is formed, but it is not possible to decide whether the osmium or the copper atom is cis to the substituent R at the C=C bond.

The vinylidene-bridged complexes **44–46** react with NaC_5H_5 or LiC_5Me_5 to give the cyclopentadienyl and pentamethylcyclopentadienyl derivatives **47–49** (Scheme VIII). They form orange or yellow-brown air-sensitive crystals which are easily soluble in all common organic solvents. Correct elemental analyses and mass spectra have been obtained. It should be noted that monomeric compounds of composition $[Cu(C_5R_5)]$ (R = H, Me) are unknown as yet and thus cannot be used directly for synthesis.[29]

The nucleophilicity of the Os=C bond in **30** has also been used to prepare the metallaheterocycle **50** (Scheme IX). Again, the osmium(0) vinylidene behaves very similar to the rhodium compound $[(C_5H_5)Rh(=C{=}CHPh)(P^iPr_3)]$.[30] We assume that the five-membered OsCNCO ring is formed by a [2 + 3] cycloaddition of benzoylnitrene, presumably generated from benzoyl azide in the coordination sphere of the metal, to the Os=C bond

(29) Stone et al. have reported that addition of CuCl to a tetrahydrofuran suspension of LiC_5Me_5 at −78 °C affords a highly reactive reagent presumed to be the complex $[Cu(C_5Me_5)(THF)]$. See: Carriedo, G. A.; Howard, J. A. K.; Stone, F. G. A. *J. Organomet. Chem.* **1983**, *250*, C28.

(30) (a) Werner, H.; Höhn, A.; Weinand, R. *J. Organomet. Chem.* **1986**, *299*, C15. (b) Höhn, A.; Werner, H. *Chem. Ber.* **1988**, *121*, 881.

of the osmium vinylidene unit. The kinetically preferred product probably is the *Z* isomer, which on warming to 60 °C in benzene solution rearranges to give the *E*-configurated derivative *E*-**50**. The course of the reaction can be followed by ^{1}H NMR spectroscopy, as during the conversion of the *Z* into the *E* isomer, a high-field shift of the signal of the exocyclic C*H*Ph proton is observed. The rearrangement possibly occurs via ring opening at the Os–O bond and intermediary formation of a zwitterionic osmium carbene species in which rotation around the C–C bond is feasible. A similar cis–trans isomerization process has been found for the rhodaheterocycle $[(C_5H_5)(P^iPr_3)RhC(=CHMe)NC(Ph)O]$.[30]

Conclusions

In this work we have described the preparation of the first half-sandwich type complexes of general composition $[(C_6H_6)Os(=C=CHR)(PR'_3)]$. The conversion of the alkynylmetal precursors $[(C_6H_6)Os(C\equiv CR)(PR'_3)X]$ into the osmium(0) vinylidenes takes place via hydrido vinyl intermediates which are formed upon treatment with $NaBH_4$ in ethanol or methanol. This method of synthesis has no precedent. Hydridovinylmetal compounds have previously been prepared either from metal dihydrides by an insertion of an alkyne into a M–H bond[8] or by inter- or intramolecular C–H activation of an olefin under the influence of a transition metal.[9] There is no direct route from the hydridovinyl complexes to the osmium(0) vinylidenes, and therefore, a metathetical displacement of the hydride by a halide ligand must be involved.

Concerning the reactivity of the vinylidene compounds $[(C_6H_6)Os(=C=CHR)(PR'_3)]$, they behave similar to the rhodium analogues $[(C_5H_5)Rh(=C=CHR)(P^iPr_3)]$.[25] In all cases studied, the Os=C rather than the C=C bond is the preferred site of attack for electrophiles. This type of behavior allows not only the preparation of osmium complexes with thio- and selenoketenes but also the synthesis of heterodinuclear vinylidene-bridged compounds of which **44**–**49** are representative examples. Recent results obtained in our laboratory on rhodium(I) vinylidenes indicate that complexes of the general type [(ring)M(=C=CHR)(L)] can also be used as vinylidene-transfer reagents, and we are presently exploring this possibility on a broader scale.

Experimental Section

All reactions were carried out under an atmosphere of argon using Schlenk tube techniques. The starting materials **1**, **2**, and **5**–**9** were prepared by published methods.[4,15] NMR spectra were recorded on JEOL FX 90 Q and on Bruker FT WH 90 and AC 200 instruments, IR spectra on a Perkin-Elmer 1420 infrared spectrophotometer, and mass spectra on a Varian MAT CH 7 instrument.

Preparation of Complexes $[(C_6H_6)Os(C\equiv CR)(P^iPr_3)I]$ (3, 4). (a) A solution of 0.70 mmol of the alkyne in 10 mL of dichloromethane was cooled to −78 °C and then quickly added to a solid mixture of **1** (480 mg, 0.70 mmol) and $AgPF_6$ (177 mg, 0.70 mmol). After being warmed to room temperature, the suspension was stirred for 30 min and then filtered. The filtrate was brought to dryness in vacuo, and the residue was dissolved in 10 mL of benzene/pentane (10:1). The solution was chromatographed on Al_2O_3 (neutral, activity grade V) using a column of 20-cm length and 20-mm diameter and benzene/pentane (10:1) as an eluant. An orange fraction was separated, which was concentrated in vacuo to ca. 5 mL. After addition of 25 mL of pentane, a yellow-orange solid precipitated. It was filtered off, repeatedly washed with pentane, and dried in vacuo, yield 237 mg (57%) for **3** and 385 mg (84%) for **4**.

(b) A second procedure for **4** is as follows: A solution of **1** (150 mg, 0.22 mmol) in 10 mL of dichloromethane was cooled to −78 °C and then treated with AgC≡CPh (46 mg, 0.22 mmol). After being warmed to room temperature, the solution was stirred for 30 min and worked up as described for part a, yield 97 mg (67%).

3. Mp: 101 °C dec. Anal. Calcd for $C_{18}H_{30}IOsP$: C, 36.36; H, 5.09; I, 21.35. Found: C, 36.68; H, 5.36; I, 21.29. MS (70 eV): *m/z* 596 (10, M^+), 469 (95, $M^+ - I$), 430 (100, $M^+ - I - C_2Me$), 391 (31, $M^+ - I - C_6H_6$). IR (KBr): ν(C≡C) 2122 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.62 (s, C_6H_6), 2.80 (m, PC*H*CH_3), 2.30 (d, J(PH) = 2.7 Hz, ≡CC*H*$_3$), 1.36 and 1.30 (both dd, J(PH) = 13.5 Hz, J(HH) = 7.0 Hz, PCHC*H*$_3$). ^{31}P NMR ($CDCl_3$): δ −6.4 (s).

4. Mp: 178 °C dec. Anal. Calcd for $C_{23}H_{32}IOsP$: C, 42.07; H, 4.91; I, 19.33. Found: C, 42.58; H, 4.92; I, 19.55. MS (70 eV): *m/z* 658 (48, M^+), 531 (100, $M^+ - I$), 453 (25, $M^+ - I - C_6H_6$), 430 (17, $M^+ - I - C_2Ph$). IR (KBr): ν(C≡C) 2085 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.24 (m, C_6H_5), 5.77 (d, J(PH) = 0.3 Hz, C_6H_6), 2.88 (m, PC*H*CH_3), 1.38 and 1.30 (both dd, J(PH) = 13.4 Hz, J(HH) = 7.2 Hz, PCHC*H*$_3$). ^{31}P NMR ($CDCl_3$): δ −4.57 (s).

Preparation of Complexes $[(C_6H_6)OsH(CH=CHR)(P^iPr_3)]$ (10, 11). (a) A suspension of 0.30 mmol of **3** in 20 mL of ethanol or of **4** in 20 mL of methanol was treated with small portions of $NaBH_4$ until the solution became nearly colorless. The solvent was removed, and the residue was extracted with benzene/pentane (1:3). The extract was brought to dryness in vacuo, and the oily residue was dissolved in 5 mL of pentane. After cooling of the solution to −78 °C, only for R = Ph light yellow crystals of **11** precipitated, which were filtered off, washed with pentane (−78 °C), and dried in vacuo, yield 134 mg (84%). For R = Me, an oily precipitate was obtained, which owing to the ^{1}H NMR spectrum consisted of ca. 95% of **10** and ca. 5% of $[(C_6H_6)OsH_2(P^iPr_3)]$ (**28**).

(b) A suspension of 0.20 mmol of **17** in 20 mL of ethanol or of **19** in 20 mL of methanol was treated with $NaBH_4$ and then worked up as described for part a. Complex **10** was obtained as a light yellow oil, yield 92 mg (91%) for **10** and 111 mg (98%) for **11**.

10. Anal. Calcd for $C_{18}H_{33}OsP$: C, 45.94; H, 7.08; Os, 40.42. Found: C, 45.73; H, 6.88; Os, 40.70. IR (KBr): ν(OsH) 2075, ν(C=C) 1587 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.70 (dddq, J(PH) = 4.4 Hz, J(HH) = 15.7, 1.2, and 1.2 Hz, OsC*H*), 5.75 (ddq, J(PH) = 2.0 Hz, J(HH) = 15.7 and 5.9 Hz, =C*H*CH_3), 4.63 (dd, J(PH) = 0.45 Hz, J(HH) = 0.4 Hz, C_6H_6), 2.02 (m, PC*H*CH_3), 1.94 (ddd, J(PH) = 1.2 Hz, J(HH) = 5.9 and 1.2 Hz, =CHC*H*$_3$), 1.07 and 1.02 (both dd, J(PH) = 12.5 Hz, J(HH) = 7.0 Hz, PCHC*H*$_3$), −9.90 (d, J(PH) = 39 Hz, Os*H*). ^{31}P NMR (C_6D_6): δ 26.7 (s, d in off-resonance).

11. Mp: 105 °C. Anal. Calcd for $C_{23}H_{35}OsP$: C, 51.86; H, 6.62; Os, 35.71. Found: C, 52.15; H, 6.88; Os, 35.40. MS (70 eV): *m/z* 534 (47, M^+), 430 (46, $M^+ - CH_2$=CHPh), 388 (92, $C_6H_6OsP^iPr_2H^+$), 346 (100, $C_6H_6OsP^iPrH_2^+$). IR (KBr): ν(OsH) 2065, ν(C=C) 1573 cm^{-1}. ^{1}H NMR (C_6D_6): δ 9.35 (ddd, J(PH) = 5.0 Hz, J(HH) = 16.5 and 1.8 Hz, OsC*H*), 7.18 (m, C_6H_5), 4.76 (d, J(HH) = 0.4 Hz, C_6H_6), 1.90 (m, PC*H*CH_3), 1.02 and 0.94 (both dd, J(PH) = 12.8 Hz, J(HH) = 6.9 Hz, PCHC*H*$_3$), −9.77 (d, J(PH) = 40 Hz, Os*H*), signal of =C*H*C_6H_5 proton masked by that of C_6H_5 protons. ^{13}C NMR (C_6D_6): δ 144.56 (s, ipso-*C* of C_6H_5), 140.81 (d, J(PC) = 3.7 Hz, =*C*HPh), 131.72 (d, J(PC) = 15.4 Hz, Os*C*H), 128.45, 124.39 and 123.55 (all s, *C*2–*C*6 of C_6H_5), 78.16 (d, J(PC) = 1.5 Hz, C_6H_6), 27.78 (d, J(PC) = 27.9 Hz, P*C*HCH$_3$), 20.37 and 19.85 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6): δ 27.5 (s, d in off-resonance).

Preparation of 11 from 4 and $NaOCH_3$. A suspension of **4** (60 mg, 0.09 mmol) in 10 mL of methanol was treated with $NaOCH_3$ (16 mg, 0.30 mmol). After the mixture was stirred for 16 h at 60 °C, the solvent was removed and the residue worked up as described above for **10** and **11**, yield 30 mg (63%).

Preparation of 11 from 19 and $NaOCH_3$. A suspension of **19** (40 mg, 0.07 mmol) in 10 mL of methanol was treated with $NaOCH_3$ (16 mg, 0.30 mmol). After the mixture was stirred for 2 h at 60 °C, the solvent was removed and the residue worked up as described above for **10** and **11**, yield 34 mg (92%).

Preparation of Complexes $[(C_6H_6)OsH(CH=CHR)(PMe^tBu_2)]$ (12–16). A suspension of 0.30 mmol of **5**–**7** in 20 mL of ethanol or of **8** and **9** in 20 mL of methanol was treated with $NaBH_4$ analogously as described for **10** and **11**. The solvent was removed, and the residue was extracted with benzene/pentane (1:1). The extract was brought to dryness in vacuo, the residue

was dissolved in 5 mL of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V). A yellow fraction was separated from which the solvent was removed in vacuo. After recrystallization from pentane (25 to −78 °C), yellow air-sensitive crystals were obtained, yield 65–75% for **12–14** and 80% for **15** and **16**.

12. Anal. Calcd for $C_{18}H_{33}OsP$: C, 45.94; H, 7.08. Found: C, 46.00; H, 7.01. MS (70 eV): m/z 472 (3, M^+), 430 (14, $M^+ - CH_2{=}CHCH_3$), 360 (54, $C_6H_6OsP^tBuH_2^+$). IR (CH_2Cl_2): ν(OsH) 2075 cm^{-1}. ^1H NMR (C_6D_6): δ 7.79 (dddq, J(PH) = 6.3 Hz, J(HH) = 15.9, 1.6, and 1.6 Hz, OsC*H*), 5.74 (ddq, J(PH) = 2.0 Hz, J(HH) = 15.9 and 6.0 Hz, =C*H*CH_3), 4.73 (dd, J(PH) = 0.2 Hz, J(HH) = 0.6 Hz, C_6H_6), 1.80 (ddd, J(PH) = 2.0 Hz, J(HH) = 6.0 and 1.6 Hz, =CHC*H*$_3$), 1.27 (d, J(PH) = 8.6 Hz, PC*H*$_3$), 1.17 and 0.97 (both d, J(PH) = 12.0 Hz, PCC*H*$_3$), −10.27 (d, J(PH) = 42 Hz, Os*H*). ^{31}P NMR (C_6D_6): δ 23.12 (s, d in off-resonance).

13. Mp: 154 °C dec. Anal. Calcd for $C_{21}H_{39}OsP$: C, 49.19; H, 7.67. Found: C, 49.68; H, 7.99. MS (70 eV): m/z 514 (15, M^+), 430 (40, $M^+ - CH_2{=}CHC_4H_9$), 360 (100, $C_6H_6OsP^tBuH_2^+$). IR (CH_2Cl_2): ν(OsH) 2080 cm^{-1}. ^1H NMR (C_6D_6): δ 7.85 (dddt, J(PH) = 4.4 Hz, J(HH) = 15.6, 1.2, and 1.2 Hz, OsC*H*), 5.81 (ddt, J(PH) = 1.9 Hz, J(HH) = 15.6 and 6.2 Hz, =C*H*R), 4.77 (dd, J(PH) = 0.3 Hz, J(HH) = 0.6 Hz, C_6H_6), 2.29 and 1.46 (both m, C_4H_9), 1.28 (d, J(PH) = 8.8 Hz, PC*H*$_3$), 1.14 and 1.03 (both d, J(PH) = 11.8 Hz, PCC*H*$_3$), −10.33 (d, J(PH) = 42 Hz, Os*H*). ^{31}P NMR (C_6D_6): δ 23.38 (s, d in off-resonance).

14. Mp: 170 °C dec. Anal. Calcd for $C_{21}H_{39}OsP$: C, 49.19; H, 7.67. Found: C, 49.20; H, 7.70. MS (70 eV): m/z 514 (14, M^+), 430 (46, $M^+ - CH_2{=}CHC_4H_9$), 360 (84, $C_6H_6OsP^tBuH_2^+$). IR (CH_2Cl_2): ν(OsH) 2075 cm^{-1}. ^1H NMR (C_6D_6): δ 7.68 (ddd, J(PH) = 4.4 Hz, J(HH) = 16.4 and 1.8 Hz, OsC*H*), 5.80 (dd, J(PH) = 2.0 Hz, J(HH) = 16.4 Hz, =C*H*R), 4.74 (dd, J(PH) = 0.2 Hz, J(HH) = 0.5 Hz, C_6H_6), 1.30 (d, J(PH) = 8.4 Hz, PC*H*$_3$), 1.17 and 1.00 (both d, J(PH) = 12.0 Hz, PCC*H*$_3$), 1.17 (s, $^tC_4H_9$), −10.40 (d, J(PH) = 42 Hz, Os*H*). ^{31}P NMR (C_6D_6): δ 23.29 (s, d in off-resonance).

15. Mp: 191 °C dec. Anal. Calcd for $C_{23}H_{35}OsP$: C, 51.86; H, 6.62. Found: C, 51.57; H, 6.75. MS (70 eV): m/z 534 (31, M^+), 430 (51, $M^+ - CH_2{=}CHPh$), 360 (100, $C_6H_6OsP^tBuH_2^+$). IR (CH_2Cl_2): ν(OsH) 2065 cm^{-1}. ^1H NMR (C_6D_6): δ 9.33 (ddd, J(PH) = 4.5 Hz, J(HH) = 16.9 and 1.6 Hz, OsC*H*), 7.16 (m, C_6H_5), 6.98 (dd, J(PH) = 2.0 Hz, J(HH) = 16.9 Hz, =C*H*Ph), 4.88 (dd, J(PH) = 0.3 Hz, J(HH) = 0.7 Hz, C_6H_6), 1.21 (d, J(PH) = 8.2 Hz, PC*H*$_3$), 1.09 and 0.96 (both d, J(PH) = 12.0 Hz, PCC*H*$_3$), −10.13 (d, J(PH) = 41 Hz, Os*H*). ^{31}P NMR (C_6D_6): δ 23.55 (s, d in off-resonance).

16. Mp: 190 °C dec. Anal. Calcd for $C_{24}H_{37}OsP$: C, 52.73; H, 6.82. Found: C, 52.29; H, 6.60. MS (70 eV): m/z 548 (29, M^+), 430 (29, $M^+ - CH_2{=}CHTol$), 360 (100, $C_6H_6OsP^tBuH_2^+$). IR (CH_2Cl_2): ν(OsH) 2062 cm^{-1}. ^1H NMR (C_6D_6): δ 9.24 (ddd, J(PH) = 4.6 Hz, J(HH) = 16.6 and 1.8 Hz, OsC*H*), 7.32 (m, C_6H_4), 6.97 (dd, J(PH) = 1.8 Hz, J(HH) = 16.6 Hz, =C*H*Tol), 4.75 (dd, J(PH) = 0.2 Hz, J(HH) = 0.4 Hz, C_6H_6), 2.21 (s, $C_6H_4CH_3$), 1.20 (d, J(PH) = 8.8 Hz, PC*H*$_3$), 1.04 and 0.93 (both d, J(PH) = 12.2 Hz, PCC*H*$_3$), −10.19 (d, J(PH) = 40 Hz, Os*H*). ^{31}P NMR (C_6D_6): δ 23.45 (s, d in off-resonance).

Preparation of [(C_6H_6)Os(CH=CHMe)(P^iPr_3)Cl] (17). A solution of **10** (141 mg, 0.30 mmol) in 5 mL of toluene was treated at 0 °C dropwise with CCl_4 (80 μL, 0.50 mmol). After being warmed to room temperature, the solution was stirred for 20 min, and then the solvent was removed. The residue was dissolved in 5 mL of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V) using benzene as eluant. A yellow fraction was separated, which was concentrated in vacuo to ca. 3 mL. After addition of 20 mL of pentane and cooling to −20 °C, a yellow microcrystalline solid precipitated. It was filtered off, repeatedly washed with pentane, and dried in vacuo, yield 137 mg (90%). Mp: 142 °C dec. Anal. Calcd for $C_{18}H_{32}ClOsP$: C, 42.80; H, 6.39; Os, 37.66. Found: C, 43.16; H, 6.34; Os, 37.90. MS (70 eV): m/z 506 (16, M^+), 470 (6, M^+ − HCl), 430 (15, M^+ − CHCl=CHMe), 428 (47, $M^+ - C_6H_6$). IR (KBr): ν(C=C) 1585 cm^{-1}. ^1H NMR (C_6D_6): δ 8.04 (ddq, J(PH) = 2.1 Hz, J(HH) = 16.2 and 1.4 Hz, OsC*H*), 5.54 (ddq, J(PH) = 2.1 Hz, J(HH) = 16.2 and 5.3 Hz, =C*H*CH_3), 4.92 (s, C_6H_6), 2.60 (m, PC*H*CH_3), 2.15 (ddd, J(PH) = 1.4 Hz, J(HH) = 5.3 and 1.4 Hz, =CHC*H*$_3$), 1.08 and 0.96 (both dd, J(PH) = 12.8 Hz, J(HH) = 7.4 Hz, PCHC*H*$_3$). ^{31}P NMR (C_6D_6): δ −1.76 (s).

Preparation of [(C_6H_6)Os(CH=CHMe)(P^iPr_3)I] (18). **18** was prepared analogously as described for **17**, starting with 0.30 mmol of **10** and 0.5 mmol of CH_2I_2. After the toluene solution was stirred for 30 min at 35 °C, it was worked up as described for **17**. Orange-yellow crystals formed, yield 168 mg (94%). Mp: 147 °C dec. Anal. Calcd for $C_{18}H_{32}IOsP$: C, 36.24; H, 5.41; I, 21.27. Found: C, 36.55; H, 5.66; I, 21.56. MS (70 eV): m/z 598 (23, M^+), 520 (37, $M^+ - C_6H_6$), 470 (44, M^+ − HI), 430 (74, M^+ − CHI=CHMe). IR (KBr): ν(C=C) 1575 cm^{-1}. ^1H NMR (C_6D_6): δ 8.75 (ddq, J(PH) = 1.7 Hz, J(HH) = 16.1 and 1.7 Hz, OsC*H*), 5.37 (ddq, J(PH) = 2.4 Hz, J(HH) = 16.1 and 6.0 Hz, =C*H*CH_3), 4.99 (s, C_6H_6), 2.10 (ddd, J(PH) = 1.7 Hz, J(HH) = 6.0 and 1.7 Hz, =CHC*H*$_3$), 2.07 (m, PC*H*CH_3), 1.06 and 0.94 (both dd, J(PH) = 12.8 Hz, J(HH) = 7.2 Hz, PCHC*H*$_3$). ^{31}P NMR (C_6D_6): δ −7.8 (s).

Preparation of [(C_6H_6)Os(CH=CHPh)(P^iPr_3)Cl] (19). **19** was prepared analogously as described for **17**, starting with 0.30 mmol of **11** and 0.50 mmol of CCl_4. A yellow microcrystalline solid was isolated, yield 87%. Mp: 154 °C dec. Anal. Calcd for $C_{23}H_{34}ClOsP$: C, 48.71; H, 6.04; Os, 33.54. Found: C, 48.31; H, 5.95; Os, 33.80. MS (70 eV): m/z 568 (6, M^+), 532 (100, M^+ − HCl), 490 (13, $M^+ - C_6H_6$), 430 (2, M^+ − CHCl=CHPh). IR (KBr): ν(C=C) 1575 cm^{-1}. ^1H NMR (C_6D_6): δ 9.39 (dd, J(PH) = 2.6 Hz, J(HH) = 16.8 Hz, OsC*H*), 7.28 (m, C_6H_5), 6.70 (dd, J(PH) = 2.4 Hz, J(HH) = 16.8 Hz, =C*H*Ph), 4.95 (s, C_6H_6), 2.59 (m, PC*H*CH_3), 1.05 and 0.92 (both dd, J(PH) = 13.5 Hz, J(HH) = 7.2 Hz, PCHC*H*$_3$). ^{13}C NMR (C_6D_6): δ 143.20 (d, J(PC) = 2.2 Hz, ipso-*C* of C_6H_5), 141.07 (d, J(PC) = 18.4 Hz, OsCH), 136.99 (d, J(PC) = 4.4 Hz, =*C*HPh), 128.68, 125.04, and 124.62 (all s, *C*2–*C*6 of C_6H_5), 81.02 (d, J(PC) = 2.9 Hz, C_6H_6), 24.85 (d, J(PC) = 26.5 Hz, P*C*HCH$_3$), 20.08 and 19.56 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6): δ −0.65 (s).

Preparation of [(C_6H_6)Os(CH=CHPh)(P^iPr_3)Br] (20). **20** was prepared analogously as described for **17**, starting with 0.30 mmol of **11** and 0.50 mmol of $CHBr_3$; the reaction temperature and time were 35 °C and 20 min. Orange-yellow crystals formed, yield 90%. Mp: 139 °C dec. Anal. Calcd for $C_{23}H_{34}BrOsP$: C, 45.17; H, 5.60; Br, 13.06. Found: C, 45.18; H, 5.32; Br, 13.14. MS (70 eV): m/z 612 (21, M^+), 534 (64, $M^+ - C_6H_6$), 532 (63, M^+ − HBr), 430 (43, M^+ − CHBr=CHPh). ^1H NMR (C_6D_6): δ 9.71 (dd, J(PH) = 2.7 Hz, J(HH) = 16.9 Hz, OsC*H*), 7.30 (m, C_6H_5), 6.72 (dd, J(PH) = 2.7 Hz, J(HH) = 16.9 Hz, =C*H*Ph), 4.98 (s, C_6H_6), 2.63 (m, PC*H*CH_3), 0.94 and 0.91 (both dd, J(PH) = 13.2 Hz, J(HH) = 7.6 Hz, PCHC*H*$_3$). ^{31}P NMR (C_6D_6): δ −2.2 (s).

Preparation of [(C_6H_6)Os(CH=CHPh)(P^iPr_3)I] (21). **21** was prepared analogously as described for **18**, starting with 0.30 mmol of **11**; orange-yellow crystals formed, yield 92%. Mp: 143 °C dec. Anal. Calcd for $C_{23}H_{34}IOsP$: C, 41.94; H, 5.20; I, 19.27. Found: C, 41.83; H, 5.23; I, 19.38. MS (70 eV): m/z 660 (29, M^+), 582 (55, $M^+ - C_6H_6$), 532 (39, M^+ − HI), 430 (62, M^+ − CHI=CHPh). IR (KBr): ν(C=C) 1575 cm^{-1}. ^1H NMR (C_6D_6): δ 10.07 (dd, J(PH) = 3.2 Hz, J(HH) = 16.9 Hz, OsC*H*), 7.18 (m, C_6H_5), 6.71 (dd, J(PH) = 2.2 Hz, J(HH) = 16.9 Hz, =C*H*Ph), 4.90 (d, J(PH) = 0.2 Hz, C_6H_6), 2.63 (m, PC*H*CH_3), 1.02 and 0.89 (both dd, J(PH) = 12.5 Hz, J(HH) = 6.2 Hz, PCHC*H*$_3$). ^{31}P NMR (C_6D_6): δ −6.62 (s).

Preparation of Complexes [(C_6H_6)Os(CH=CHR)(PMe^tBu_2)Cl] (22–26). A solution of 0.30 mmol of **12–16** in 5 mL of toluene was treated dropwise at −20 °C with CCl_4 (80–100 μL, 0.50–0.62 mmol) and then under stirring warmed slowly (ca. 45 min) to 0 °C. The solvent was removed in vacuo, the residue was dissolved in 3 mL of dichloromethane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V) using C_6H_6/CH_2Cl_2 (1:1) as eluant. An orange or yellow fraction was separated, which was concentrated to ca. 3 mL in vacuo. After addition of 20 mL of pentane, orange or yellow solids precipitated, which were filtered off, repeatedly washed with pentane, and dried in vacuo, yield 80–90%.

22. Mp: 121 °C dec. Anal. Calcd for $C_{18}H_{32}ClOsP$: C, 42.80; H, 6.39. Found: C, 42.45; H, 6.01. MS (70 eV): m/z 506 (14, M^+), 470 (12, M^+ − HCl), 430 (33, M^+ − CHCl=CHMe), 428 (40, $M^+ - C_6H_6$). ^1H NMR ($CDCl_3$): δ 7.56 (ddq, J(PH) = 3.0 Hz, J(HH) = 16.3 and 1.6 Hz, OsC*H*), 5.83 (ddq, J(PH) = 2.5 Hz, J(HH) = 16.3 and 5.4 Hz, =C*H*CH_3), 5.42 (d, J(PH) = 0.3 Hz, C_6H_6), 1.75 (ddd, J(PH) = 1.4 Hz, J(HH) = 5.4 and 1.6 Hz, =CHC*H*$_3$), 1.28 (d, J(PH) = 9.4 Hz, PC*H*$_3$), 1.36 and 1.14 (both

d, J(PH) = 12.3 Hz, PCCH_3). ^{31}P NMR ($CDCl_3$): δ 4.14 (s).

23. Mp: 142 °C dec. Anal. Calcd for $C_{21}H_{38}ClOsP$: C, 46.10; H, 7.00. Found: C, 45.81; H, 7.14. MS (70 eV): m/z 548 (19, M^+), 512 (67, M^+ - HCl), 470 (31, M^+ - C_6H_6), 430 (37, M^+ - CHCl=CH^{n}Bu). ^{1}H NMR (C_6D_6): δ 8.01 (ddt, J(PH) = 3.4 Hz, J(HH) = 16.3 and 2.5 Hz, OsCH), 5.88 (ddt, J(PH) = 2.6 Hz, J(HH) = 16.3 and 6.2 Hz, =CHC$_4$H$_9$), 5.04 (d, J(PH) = 0.3 Hz, C_6H_6), 2.44 and 1.53 (both m, C_4H_9), 1.33 (d, J(PH) = 8.9 Hz, PCH_3), 1.17 and 0.94 (both d, J(PH) = 12.0 Hz, PCCH_3). ^{31}P NMR (C_6D_6): δ 4.21 (s).

***E*/*Z*-24.** Mp: 140 °C dec. Anal. Calcd for $C_{21}H_{38}ClOsP$: C, 46.10; H, 7.00. Found: C, 46.00; H, 7.01. MS (70 eV): m/z 548 (6, M^+), 512 (60, M^+ - HCl), 470 (36, M^+ - C_6H_6), 430 (40, M^+ - CHCl=CH^{t}Bu).

***E*-24.** ^{1}H NMR (C_6D_6): δ 7.81 (dd, J(PH) = 2.8 Hz, J(HH) = 16.8 Hz, OsCH), 5.78 (dd, J(PH) = 2.4 Hz, J(HH) = 16.8 Hz, =CHC$_4$H$_9$), 4.98 (s, C_6H_6), 1.28 (d, J(PH) = 9.1 Hz, PCH_3), 1.14 (s, ^{t}C$_4H_9$), 1.17 and 0.93 (both d, J(PH) = 12.0 Hz, PCCH_3). ^{13}C NMR (C_6D_6): δ 146.48 (d, J(PC) = 16.7 Hz, OsCH), 123.23 (d, J(PC) = 4.3 Hz, =CHR), 81.36 (d, J(PC) = 2.8 Hz, C_6H_6), 39.49 and 38.38 (both d, J(PC) = 24.4 and 19.7 Hz, PCCH$_3$), 36.37 (s, C(CH$_3$)$_3$), 30.76 and 30.70 (both s, PCCH_3), 30.59 (s, C(CH$_3$)$_3$), 3.84 (d, J(PC) = 30.8 Hz, PCH$_3$). ^{31}P NMR (C_6D_6): δ 4.25 (s).

***Z*-24.** ^{1}H NMR (C_6D_6): δ 8.52 (dd, J(PH) = 3.8 Hz, J(HH) = 6.9 Hz, OsCH), 5.91 (dd, J(PH) = 2.4 Hz, J(HH) = 6.9 Hz, =CHC$_4$H$_9$), 5.09 (s, C_6H_6), 1.54 (d, J(PH) = 9.0 Hz, PCH_3), 1.19 (s, ^{t}C$_4H_9$), 1.18 and 0.90 (both d, J(PH) = 12.6 Hz, PCCH_3). ^{13}C NMR (C_6D_6): δ 149.45 (d, J(PC) = 16.8 Hz, OsCH), 113.88 (d, J(PC) = 4.6 Hz, =CHR), 81.06 (s, C_6H_6), 38.73 and 37.82 (both d, J(PC) = 22.8 Hz, PCCH$_3$), 36.62 (s, C(CH$_3$)$_3$), 31.45 and 31.39 (both s, PCCH_3), 30.92 (s, C(CH$_3$)$_3$), 9.76 (d, J(PC) = 31.7 Hz, PCH$_3$). ^{31}P NMR (C_6D_6): δ 4.27 (s).

25. Mp: 150 °C dec. Anal. Calcd for $C_{23}H_{34}ClOsP$: C, 48.71; H, 6.04. Found: C, 48.60; H, 6.22. MS (70 eV): m/z 568 (11, M^+), 532 (100, M^+ - HCl), 490 (13, M^+ - C_6H_6), 430 (7, M^+ - CHCl=CHPh). ^{1}H NMR (C_6D_6): δ 9.32 (dd, J(PH) = 3.1 Hz, J(HH) = 17.1 Hz, OsCH), 7.16 (m, C_6H_5), 5.01 (d, J(PH) = 0.3 Hz, C_6H_6), 1.24 (d, J(PH) = 9.4 Hz, PCH_3), 1.14 and 0.84 (both d, J(PH) = 12.2 Hz, PCCH_3), signal of =CHPh proton masked by that of the C_6H_5 protons. ^{31}P NMR (C_6D_6): δ 4.41 (s).

26. Mp: 149 °C dec. Anal. Calcd for $C_{24}H_{36}ClOsP$: C, 49.60; H, 6.24. Found: C, 49.02; H, 6.20. MS (70 eV): m/z 582 (10, M^+), 546 (100, M^+ - HCl), 504 (10, M^+ - C_6H_6), 430 (15, M^+ - CHCl=CHTol). ^{1}H NMR (C_6D_6): δ 9.17 (dd, J(PH) = 3.0 Hz, J(HH) = 17.1 Hz, OsCH), 7.29 (m, C_6H_4), 4.99 (d, J(PH) = 0.3 Hz, C_6H_6), 2.17 (s, $C_6H_4CH_3$), 1.24 (d, J(PH) = 9.6 Hz, PCH_3), 1.18 and 0.93 (both d, J(PH) = 12.1 Hz, PCCH_3), signal of = CHTol proton masked by that of the C_6H_4 protons. ^{31}P NMR (C_6D_6): δ 4.39 (s).

Preparation of [(C_6H_6)Os(O_2CCF_3)$_2$(P^iPr_3)] (27). A suspension of **1** (410 mg, 0.60 mmol) in 15 mL of benzene was treated with CF_3CO_2Ag (398 mg, 1.80 mmol) and stirred for 1 h at room temperature. The solution was filtered, and the filtrate was brought to dryness in vacuo. The residue was dissolved in 3 mL of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V). With benzene, a yellow fraction was eluted, which was concentrated to ca. 5 mL in vacuo. After addition of 20 mL of pentane and cooling to 0 °C, a light yellow solid precipitated. It was filtered off, repeatedly washed with pentane, and dried in vacuo, yield 208 mg (53%). Mp: 167 °C dec. Anal. Calcd for $C_{19}H_{27}F_6O_4OsP$: C, 34.86; H, 4.16. Found: C, 35.45; H, 4.58. IR (KBr): ν(C=O) 1695, ν(C—O) 1188, ν(CF_3) 1133 cm^{-1}. ^{1}H NMR (C_6D_6): δ 5.60 (d, J(PH) = 0.4 Hz, C_6H_6), 2.07 (m, PCHCH$_3$), 0.87 (dd, J(PH) = 13.6 Hz, J(HH) = 6.8 Hz, PCHCH_3). ^{31}P NMR (C_6D_6): δ 9.8 (s).

Reaction of 27 with BrMgCH=CHPh. A suspension of **27** (100 mg, 0.16 mmol) in 10 mL of benzene was treated with 0.25 mL of a 0.82 M solution of BrMgCH=CHPh in THF. An immediate color change from light yellow to deep red occurred. The reaction mixture was stirred for 1 h at 60 °C and then cooled to room temperature and filtered. The filtrate was brought to dryness in vacuo, the residue was dissolved in 5 mL of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V). With benzene, an orange-yellow fraction was eluted, which according to the ^{1}H NMR spectrum contained **20** and small amounts of [(C_6H_6)OsH_2(P^iPr_3)] (**28**). With CH_2Cl_2, a second orange-red fraction was obtained, which was separated and concentrated to ca. 2 mL in vacuo. After addition of 10 mL of pentane, a red solid precipitated, which was shown by ^{1}H NMR spectroscopy to be **29**, yield 22 mg (23%).

Preparation of [(C_6H_6)OsBr_2(P^iPr_3)] (29). A solution of **27** (50 mg, 0.08 mmol) in 10 mL of dichloromethane was treated with KBr (60 mg, 0.50 mmol) and stirred for 20 min at room temperature. The solution was filtered, and the filtrate was concentrated to ca. 2 mL in vacuo. After addition of 20 mL of pentane, a deep red solid precipitated, which was filtered off, repeatedly washed with pentane, and dried in vacuo, yield 44 mg (94%). Mp: 184 °C dec. Anal. Calcd for $C_{15}H_{27}Br_2OsP$: C, 30.62; H, 4.63. Found: C, 31.37; H, 4.40. ^{1}H NMR ($CDCl_3$): δ 6.10 (d, J(PH) = 0.4 Hz, C_6H_6), 3.01 (m, PCHCH$_3$), 1.37 (dd, J(PH) = 13.6, J(HH) = 7.0 Hz, PCHCH_3). ^{31}P NMR ($CDCl_3$): δ -10.2 (s).

Preparation of [(C_6H_6)Os(=C=CHPh)(P^iPr_3)] (30). A suspension of 0.5 mmol of **19**, **20**, or **21** in 10 mL of ether was treated dropwise at -40 °C with a 1.6 M solution of *tert*-butyllithium in pentane until a clear red-violet solution was obtained. After the solution was cooled to -78 °C, 100 μL of methanol was added to destroy excess of ^{t}BuLi. The solution was then warmed to room temperature, and the solvent was removed. The residue was extracted with 25 mL of pentane, and the extract was brought to dryness in vacuo. The residue was dissolved in 3 mL of benzene, and the solution was chromatographed on Al_2O_3 (basic, activity grade V) using a short column (ca. 1 cm) with a diameter of 10 mm. With benzene, a yellow-brown fraction was eluted from which the solvent was removed in vacuo. After recrystallization from pentane (25 to -78 °C), yellow-brown crystals were obtained, yield 241 mg (91%). Mp: 118 °C dec. Anal. Calcd for $C_{23}H_{33}OsP$: C, 52.05; H, 6.27; Os, 35.84. Found: C, 52.44; H, 6.61; Os, 36.10. MS (70 eV): m/z 532 (82, M^+), 430 (4, M^+ - C_2HPh). IR (KBr): ν(C=C) 1568 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.16 (m, C_6H_5), 4.88 (s, C_6H_6), 3.14 (d, J(PH) = 6.4 Hz, =CHPh), 2.09 (m, PCHCH$_3$), 1.03 and 0.99 (both dd, J(PH) = 13.3 Hz, J(HH) = 7.1 Hz, PCHCH_3). ^{13}C NMR (C_6D_6): δ 278.30 (d, J(PC) = 22.2 Hz, Os=C), 134.61 (d, J(PC) = 4.3 Hz, ipso-C of C_6H_5), 127.87, 124.52, and 122.48 (all s, $C2$–$C6$ of C_6H_5), 110.91 (d, J(PC) = 5.2 Hz, =CHPh), 77.00 (d, J(PC) = 2.6 Hz, C_6H_6), 26.97 (d, J(PC) = 27.6 Hz, PCHCH$_3$), 20.24 and 19.94 (both s, PCHCH$_3$). ^{31}P NMR (C_6D_6): δ 35.5 (s).

Preparation of Complexes [(C_6H_6)Os(=C=CHR)(PMe^tBu_2)] (31–33). These compounds were prepared analogously as described for **30**, using 0.30 mmol of **23**, **25**, or **26** as starting material. Yellow-brown crystals were obtained from pentane, yield 75 mg (49%) for **31**, 118 mg (74%) for **32**, and 113 mg (69%) for **33**.

31. Mp: >100 °C dec. Anal. Calcd for $C_{21}H_{37}OsP$: C, 49.39; H, 7.30. Found: C, 49.90; H, 7.70. MS (70 eV): m/z 512 (14, M^+), 430 (2, M^+ - $C_2HC_4H_9$), 360 (100, $C_6H_6OsP^tBuH_2^+$). IR (C_6H_6): ν(C=C) 1555 cm^{-1}. ^{1}H NMR (C_6D_6): δ 5.01 (s, C_6H_6), 2.73, 1.66, and 1.03 (all m, C_4H_9), 2.25 (dt, J(PH) = 6.0, J(HH) = 6.1 Hz, =CHR), 1.24 and 1.23 (both d, J(PH) = 13.0 Hz, PCCH_3), 1.13 (d, J(PH) = 9.9 Hz, PCH_3).

32. Mp: 112 °C dec. Anal. Calcd for $C_{23}H_{33}OsP$: C, 52.05; H, 6.27. Found: C, 52.00; H, 6.07. MS (70 eV): m/z 532 (40, M^+), 430 (9, M^+ - C_2HPh), 360 (100, $C_6H_6OsP^tBuH_2^+$). IR (C_6H_6): ν(C=C) 1565 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.21 (m, C_6H_5), 4.85 (s, C_6H_6), 3.30 (d, J(PH) = 6.2 Hz, =CHPh), 1.14 and 1.13 (both d, J(PH) = 13.1 Hz, PCCH_3), 1.04 (d, J(PH) = 9.4 Hz, PCH_3). ^{13}C NMR (C_6D_6): δ 277.47 (d, J(PC) = 21.2 Hz, Os=C), 135.36 (d, J(PC) = 3.8 Hz, ipso-C of C_6H_5), 129.35, 128.61 and 124.97 (all s, $C2$–$C6$ of C_6H_5), 112.24 (d, J(PC) = 4.2 Hz, =CHPh), 77.41 (d, J(PC) = 2.4 Hz, C_6H_6), 39.97 and 39.42 (both d, J(PC) = 25.2 and 23.1 Hz, PCCH$_3$), 29.89 and 29.61 (both s, PCCH_3), 12.26 (d, J(PC) = 30.2 Hz, PCH$_3$).

33. Mp: 109 °C dec. Anal. Calcd for $C_{24}H_{35}OsP$: C, 52.92; H, 6.48. Found: C, 53.00; H, 6.88. MS (70 eV): m/z 546 (31, M^+), 430 (7, M^+ - C_2HTol), 360 (100, $C_6H_6OsP^tBuH_2^+$). IR (C_6H_6): ν(C=C) 1570 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.24 (m, C_6H_4), 4.97 (s, C_6H_6), 3.45 (d, J(PH) = 6.1 Hz, =CHTol), 2.43 (s, $C_6H_4CH_3$), 1.29 and 1.28 (both d, J(PH) = 13.6 Hz, PCCH_3), 1.10 (d, J(PH) = 9.7 Hz, PCH_3).

Reaction of Vinylidene Complexes 30–33 with HCl. A solution of 0.10 mmol **30**–**33** in 5 mL of pentane was treated dropwise at -78 °C with 0.26 mL of a 0.38 M solution of HCl in

benzene. After careful warming to room temperature (ca. 45 min), the obtained precipitate was separated from the mother liquor, repeatedly washed with pentane, and then shown by ^{1}H NMR spectroscopy to be identical with **19**, **23**, **25**, and **26**, yield 90–95%.

Preparation of [$(C_6H_6)OsCl_2(P^iPr_3)$] (34) from 30 and Excess HCl. If a solution of **30** (53 mg, 0.10 mmol) was not treated with an equimolar amount but with an excess of HCl in benzene, a yellow solid precipitated. It was filtered off, washed with pentane, and recrystallized from CH_2Cl_2/pentane, yield 26 mg (52%). Mp: 174 °C dec. Anal. Calcd for $C_{15}H_{27}Cl_2OsP$: C, 36.07; H, 5.45. Found: C, 35.76; H, 5.32. MS (70 eV): m/z 500 (42, M^+), 422 (39, $M^+ - C_6H_6$), 340 (100, $M^+ - P^iPr_3$). ^{1}H NMR ($CDCl_3$): δ 6.04 (s, C_6H_6), 2.89 (m, PC*H*CH_3), 1.36 (dd, J(PH) = 13.5, J(HH) = 7.2 Hz, PCHC*H*$_3$). ^{31}P NMR ($CDCl_3$): δ −4.0 (s).

Preparation of [$(C_6H_6)Os(CH{=}CHPh)(P^iPr_3)(O_2CCF_3)$] (35). A solution of **30** (249 mg, 0.47 mmol) in 10 mL of pentane was treated dropwise at −78 °C with CF_3CO_2H (35 μL, 0.47 mmol). After being warmed to room temperature, the solution was vigorously stirred for 20 min. The precipitate was filtered off, washed with pentane, and recrystallized from benzene/pentane to give light yellow crystals, yield 203 mg (67%). Mp: 129 °C dec. Anal. Calcd for $C_{25}H_{34}F_3O_2OsP$: C, 46.57; H, 5.32; Os, 29.50. Found: C, 46.62; H, 5.03; Os, 29.70. MS (70 eV): m/z 646 (1, M^+), 568 (1, $M^+ - C_6H_6$), 532 (90, $M^+ - CF_3CO_2H$), 430 (3, $C_6H_6OsP^iPr_3^+$). IR (KBr): ν(C=O) 1686, ν(C=C) 1578, ν(C−O) 1187 cm^{-1}. ^{1}H NMR (C_6D_6): δ 8.58 (dd, J(PH) = 2.2, J(HH) = 16.6 Hz, OsC*H*), 7.13 (m, C_6H_5), 6.55 (dd, J(PH) = 2.2, J(HH) = 16.6 Hz, CH=C*H*Ph), 5.12 (s, C_6H_6), 2.16 (m, PC*H*CH_3), 0.86 and 0.80 (both dd, J(PH) = 13.1, J(HH) = 7.1 Hz, PCHC*H*$_3$). ^{31}P NMR (C_6D_6): δ 5.93 (s).

Reaction of 35 with NaI. A solution of **35** (64 mg, 0.10 mmol) and NaI (30 mg, 0.20 mmol) in 10 mL of acetone was stirred for 10 min at room temperature. The solvent was removed in vacuo and the residue worked up as described before. The orange solid obtained from benzene/pentane was shown by ^{1}H NMR spectroscopy to be identical with **21**, yield 61 mg (93%).

Preparation of [$(C_6H_6)(P^iPr_3)Os(o\text{-}C_6H_4)CH{=}CH$] (36). A suspension of **35** (80 mg, 0.12 mmol) in 10 mL of methanol was stirred for 1 h at room temperature. The solvent was removed in vacuo, the residue was dissolved in 5 mL of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V). With benzene, a yellow fraction was eluted. It was concentrated to ca. 2 mL in vacuo, and then pentane (20 mL) was added. A yellow solid precipitated, which was filtered off, repeatedly washed with pentane, and dried in vacuo, yield 28 mg (45%). Mp: 138 °C dec. Anal. Calcd for $C_{23}H_{33}OsP$: C, 52.05; H, 6.27. Found: C, 52.15; H, 6.55. MS (70 eV): m/z 532 (81, M^+). IR (KBr): ν(C=C) 1573 cm^{-1}. ^{1}H NMR (C_6D_6): δ 9.43 (dd, J(PH) = 2.5, J(HH) = 17.0 Hz, OsC*H*), 7.16 (m, C_6H_4), 6.72 (dd, J(PH) = 2.5, J(HH) = 17.0 Hz, OsCH=C*H*–), 4.95 (s, C_6H_6), 2.50 (m, PC*H*CH_3), 0.93 and 0.86 (dd, J(PH) = 13.1, J(HH) = 7.2 Hz, PCHC*H*$_3$). ^{31}P NMR (C_6D_6): δ −0.61 (s).

Preparation of Complexes [$(C_6H_6)Os(CI{=}CHR)(PMe^tBu_2)I$] (37, 38). A solution of **32** and **33** (0.30 mmol) in 8 mL of ether was treated slowly at −78 °C with a solution of iodine (76 mg, 0.30 mmol) in 7 mL of ether. After the mixture was warmed to room temperature, the yellow precipitate was separated, repeatedly washed with pentane, and dried in vacuo, yield 167 mg (71%) for **37** and 157 mg (66%) for **38**.

37. Mp: 89 °C dec. Anal. Calcd for $C_{23}H_{33}I_2OsP$: C, 35.21; H, 4.24. Found: C, 35.73; H, 4.59. MS (70 eV): m/z 786 (2, M^+), 659 (73, $M^+ - I$), 581 (44, $M^+ - C_6H_6 - I$), 430 (63, $C_6H_6OsPMe^tBu_2^+$). ^{1}H NMR ($CDCl_3$): δ 7.31 (m, C_6H_5), 7.05 (d, J(PH) = 2.8 Hz, CI=C*H*R), 5.79 (s, C_6H_6), 2.01 (d, J(PH) = 9.6 Hz, PC*H*$_3$), 1.40 and 1.32 (both d, J(PH) = 12.7 Hz, PCC*H*$_3$).

38. Mp: 93–94 °C dec. Anal. Calcd for $C_{24}H_{35}I_2OsP$: C, 36.10; H, 4.42. Found: C, 36.51; H, 4.90. MS (70 eV): m/z 673 (34, $M^+ - I$), 595 (23, $M^+ - C_6H_6 - I$), 430 (63, $C_6H_6OsPMe^tBu_2^+$). ^{1}H NMR ($CDCl_3$): δ 7.16 (m, C_6H_4), 5.69 (s, C_6H_6), 2.28 (s, $C_6H_4CH_3$), 1.98 (d, J(PH) = 9.4 Hz, PC*H*$_3$), 1.41 and 1.30 (both d, J(PH) = 12.8 Hz, PCC*H*$_3$), signal of CI=C*H*I not exactly located.

Preparation of Complexes [$(C_6H_6)Os(C{\equiv}CR)(PMe^tBu_2)I$] (8, 9) from 37 and 38. A solution of 0.10 mmol of **37** and **38** in 2 mL of dichloromethane was chromatographed on Al_2O_3 (neutral, activity grade V). With CH_2Cl_2, an orange-yellow fraction was eluted, which was brought to dryness in vacuo. It was shown by IR and ^{1}H NMR spectroscopy to be identical with **8** and **9**, yield 80%.

Preparation of Complexes [$(C_6H_6)Os(\eta^2\text{-}E{=}C{=}CHPh)(P^iPr_3)$] (39, 40). A solution of **30** (150 mg, 0.28 mmol) in 10 mL of benzene was treated with sulfur (9 mg, 0.28 mmol) or selenium (23 mg, 0.28 mmol), respectively. The solution was stirred for 45 min at room temperature, then concentrated to ca. 5 mL, and chromatographed on Al_2O_3 (neutral, activity grade V). With benzene, a dark yellow (**39**) or red (**40**) fraction was eluted, which was brought to dryness in vacuo. The residue was extracted with 25 mL of pentane, and the pentane solution was concentrated to ca. 5 mL. After the solution was stored at −20 °C, brown-yellow (**39**) or deep red (**40**) crystals were obtained, yield 97 mg (62%) for **39** and 135 mg (79%) for **40**.

39. Mp: 148 °C dec. Anal. Calcd for $C_{23}H_{33}OsPS$: C, 49.06; H, 5.91; Os, 33.80; S, 5.70. Found: C, 48.52; H, 5.76; Os, 34.10; S, 5.85. MS (70 eV): m/z 564 (77, M^+), 532 (22, $M^+ - S$), 484 (30, $M^+ - C_6H_6 - H_2$). IR (KBr): ν(C=C) 1575 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.35 (m, C_6H_5), 4.78 (d, J(PH) = 4.0 Hz, C=C*H*Ph), 4.75 (s, C_6H_6), 1.90 (m, PC*H*CH_3), 0.84 and 0.81 (both dd, J(PH) = 12.8, J(HH) = 7.1 Hz, PCHC*H*$_3$). ^{31}P NMR (C_6D_6): δ 15.0 (s).

40. Mp: 141 °C dec. Anal. Calcd for $C_{23}H_{33}OsPSe$: C, 45.31; H, 5.46; Se, 12.95. Found: C, 45.70; H, 5.53; Se, 13.10. MS (70 eV): m/z 612 (19, M^+), 532 (97, $M^+ - Se$). IR (KBr): ν(C=C) 1578 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.50 (m, C_6H_5), 4.89 (d, J(PH) = 4.8 Hz, C=C*H*Ph), 4.85 (d, J(PH) = 0.2 Hz, C_6H_6), 2.08 (m, PC*H*CH_3), 0.95 and 0.90 (both dd, J(PH) = 13.0, J(HH) = 7.1 Hz, PCHC*H*$_3$). ^{31}P NMR (C_6D_6): δ 12.3 (s).

Preparation of [$(C_6H_6)Os(\eta^2\text{-}S{=}C{=}CHPh)(PMe^tBu_2)$] (41). A solution of **32** (159 mg, 0.30 mmol) in 10 mL of benzene was treated with sulfur (9.7 mg, 0.30 mmol) and stirred for 30 min at room temperature. The solution was concentrated to ca. 2 mL and chromatographed on Al_2O_3 (neutral, activity grade V). The dark brown fraction which was eluted with benzene was brought to dryness in vacuo and the residue recrystallized from pentane to give brown air-stable crystals, yield 86 mg (51%). Mp: 140 °C. Anal. Calcd for $C_{23}H_{33}OsPS$: C, 49.06; H, 5.91. Found: C, 49.00; H, 5.89. MS (70 eV): m/z 564 (41, M^+), 532 (20, $M^+ - S$), 360 (100, $C_6H_6OsP^tBuH_2^+$). IR (CH_2Cl_2): ν(C=C) 1575 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.35 (m, C_6H_5), 4.77 (s, C_6H_6), 4.60 (d, J(PH) = 4.1 Hz, C=C*H*Ph), 1.90 (d, J(PH) = 9.1 Hz, PC*H*$_3$), 1.30 and 1.14 (both d, J(PH) = 12.9 Hz, PCC*H*$_3$).

Preparation of Complexes [$(C_6H_6)Os(\eta^2\text{-}Se{=}C{=}CHR)(PMe^tBu_2)$] (42, 43). A solution of **31** (117 mg, 0.23 mmol) or **32** (122 mg, 0.23 mmol) in 10 mL of benzene was treated with red selenium (31.5 mg, 0.40 mmol) and stirred for 45 min at room temperature. The reaction mixture was worked up as described for **41**. Red, moderately air-stable crystals were obtained, yield 35 mg (26%) for **42** and 56 mg (40%) for **43**.

42. Anal. Calcd for $C_{21}H_{36}OsPSe$: C, 42.85; H, 6.16. Found: C, 42.39; H, 5.99. MS (70 eV): m/z 591 (14, M^+), 511 (51, $M^+ - Se$), 360 (100, $C_6H_6OsP^tBuH_2^+$). IR (CH_2Cl_2): ν(C=C) 1570 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.31 (s, C_6H_6), 1.96 (d, J(PH) = 9.5 Hz, PC*H*$_3$), 1.28 and 1.17 (both d, J(PH) = 12.9 Hz, PCC*H*$_3$), 0.95 (m, C_4H_9), signal of C=C*H*R not exactly located.

43. Mp: 137 °C dec. Anal. Calcd for $C_{23}H_{33}OsPSe$: C, 45.31; H, 5.46. Found: C, 45.81; H, 5.89. MS (70 eV): m/z 612 (20, M^+), 532 (81, $M^+ - Se$), 360 (100, $C_6H_6OsP^tBuH_2^+$). IR (CH_2Cl_2): ν(C=C) 1580 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.40 (m, C_6H_5), 4.88 (s, C_6H_6), 4.84 (d, J(PH) = 4.5 Hz, C=C*H*Ph), 1.99 (d, J(PH) = 9.3 Hz, PC*H*$_3$), 1.32 and 1.12 (both d, J(PH) = 13.0 Hz, PCC*H*$_3$).

Preparation of [$(C_6H_6)(P^iPr_3)Os(\mu\text{-}C{=}CHPh)CuCl$] (44). A solution of **30** (100 mg, 0.18 mmol) in 10 mL of THF was treated with CuCl (19 mg, 0.20 mmol) and stirred at 40 °C for 30 min. After the mixture was cooled to room temperature, the solvent was removed, and the residue was dissolved in 10 mL of CH_2Cl_2. The solution was filtered, and the filtrate was concentrated to ca. 5 mL and then chromatographed on Al_2O_3 (neutral, activity grade V). With CH_2Cl_2, a yellow fraction was eluted. It was concentrated to ca. 2 mL, and then pentane (20 mL) was added. A yellow solid precipitated, which was separated from the mother liquor, repeatedly washed with pentane, and dried in vacuo, yield 93 mg (82%). Mp: 111 °C dec. Anal. Calcd for $C_{23}H_{33}ClCuOsP$: C, 43.87; H, 5.28; Cu, 10.09. Found: C, 43.74; H, 5.41; Cu, 9.85.

MS (70 eV): m/z 630 (3, M^+), 532 (92, M^+ - CuCl). IR (KBr): ν(C=C) 1575 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.08 (m, C_6H_5), 5.64 (d, J(PH) = 0.3 Hz, C_6H_6), 4.12 (d, J(PH) = 5.8 Hz, C=CHPh), 2.35 (m, PCHCH_3), 1.24 and 1.13 (both dd, J(PH) = 13.7 Hz, J(HH) = 7.0 Hz, PCHCH_3). ^{13}C NMR ($CDCl_3$): δ 270.59 (d, J(PC) = 30.9 Hz, OsCCu), 132.94 (s, =CHPh), 128.72 (s, ipso-C of C_6H_5), 128.37, 127.74 and 126.48 (all s, C2–C6 of C_6H_5), 79.60 (s, C_6H_6), 25.32 (d, J(PC) = 25.8 Hz, $PCHCH_3$), 20.64 and 20.29 (both s, $PCHCH_3$). ^{31}P NMR ($CDCl_3$): δ 28.1 (s).

Preparation of Complexes [(C_6H_6)(PMe^tBu_2)Os(μ-C=CHR)CuCl] (45, 46). These compounds were prepared analogously as described for **44** but using 0.30 mmol of **31** or **32** as starting material. It was observed that depending on the conditions the yellow solid which precipitated after pentane was added to the dichloromethane solution contained a substance which was insoluble in CH_2Cl_2 or $CHCl_3$ but had the same composition as **45** or **46**, yield 112 mg (62%) for **45** and 119 mg (63%) for **46**.

45. Anal. Calcd for $C_{21}H_{37}ClCuOsP$: C, 41.37; H, 6.12. Found: C, 41.01; H, 5.88. ^1H NMR ($CDCl_3$): δ 5.54 (s, C_6H_6), 2.95 (m, C=CHC_4H_9), 2.17 and 0.90 (both m, C_4H_9), 1.63 (d, J(PH) = 8.3 Hz, PCH_3), 1.22 and 1.21 (both d, J(PH) = 13.2 Hz, $PCCH_3$).

46. Anal. Calcd for $C_{23}H_{33}ClCuOsP$: C, 43.87; H, 5.28; Cu, 10.09. Found: C, 43.37; H, 5.01; Cu, 9.79. MS (70 eV): m/z 630 (2, M^+), 532 (40, M^+ - CuCl). ^1H NMR ($CDCl_3$): δ 7.17 (m, C_6H_5), 5.56 (d, J(PH) = 0.2 Hz, C_6H_6), 4.03 (d, J(PH) = 5.2 Hz, C=CHPh), 1.52 (d, J(PH) = 8.1 Hz, PCH_3), 1.27 and 1.08 (both d, J(PH) = 13.5 Hz, $PCCH_3$).

Preparation of [(C_6H_6)(P^iPr_3)Os(μ-C=CHPh)Cu(C_5H_5)] (47). A solution of **44** (126 mg, 0.20 mmol) in 10 mL of THF was treated with NaC_5H_5 (18 mg, 0.20 mmol) and stirred for 30 min at room temperature. The solvent was removed, and the residue was extracted with 25 mL of pentane. The pentane solution was concentrated to ca. 3 mL in vacuo and then cooled to -20 °C to give orange crystals, yield 117 mg (89%). Mp: 79 °C dec. Anal. Calcd for $C_{28}H_{38}CuOsP$: C, 51.01; H, 5.81; Cu, 9.64. Found: C, 50.82; H, 6.04; Cu, 9.66. IR (KBr): ν(C=C) 1572 cm^{-1}. ^1H NMR (C_6D_6): δ 7.23 (m, C_6H_5), 6.34 (s, C_5H_5), 5.65 (d, J(PH) = 4.1 Hz, C=CHPh), 4.96 (s, C_6H_6), 1.91 (m, PCHCH_3), 0.98 and 0.89 (both dd, J(PH) = 13.3 Hz, J(HH) = 7.5 Hz, $PCHCH_3$). ^{13}C NMR (C_6D_6): δ 249.64 (d, J(PC) = 14.1 Hz, OsCCu), 135.84 (s, =CHPh), 128.54 (s, ipso-C of C_6H_5), 128.15, 125.39 and 124.16 (all s, C2–C6 of C_6H_5), 99.59 (s, C_5H_5), 78.48 (s, C_6H_6), 28.31 (d, J(PC) = 28.2 Hz, $PCHCH_3$), 21.18 and 20.26 (both s, $PCHCH_3$). ^{31}P NMR (C_6D_6): δ 22.8 (s).

Preparation of [(C_6H_6)(PMe^tBu_2)Os(μ-C=CH$^nC_4H_9$)Cu(C_5H_5)] (48). This compound was prepared analogously as described for **47** but using 0.30 mmol of **45** as starting material. Orange air-sensitive crystals were produced, yield 119 mg (62%). Mp: 80 °C dec. Anal. Calcd for $C_{26}H_{42}CuOsP$: C, 48.85; H, 6.62. Found: C, 48.36; H, 6.40. ^1H NMR ($CDCl_3$): δ 6.15 (s, C_5H_5), 4.99 (s, C_6H_6), 2.74 (m, C=CHC_4H_9), 1.94 and 0.74 (both m, C_4H_9), 1.28 (d, J(PH) = 8.5 Hz, PCH_3), 1.02 and 0.88 (both d, J(PH) = 14.1 Hz, $PCCH_3$).

Preparation of [(C_6H_6)(PMe^tBu_2)Os(μ-C=CHPh)Cu(C_5Me_5)] (49). A solution of **46** (126 mg, 0.20 mmol) in 10 mL of THF was treated with LiC_5Me_5 (35.5 mg, 0.25 mmol) and stirred for 30 min at room temperature. The reaction mixture was worked up as described for **47**. Orange crystals formed, yield 66 mg (45%). Mp: 71 °C dec. Anal. Calcd for $C_{33}H_{48}CuOsP$: C, 54.33; H, 6.63; Cu, 8.71. Found: C, 53.80; H, 6.23; Cu, 8.31. ^1H NMR ($CDCl_3$): δ 7.29 (m, C_6H_5), 5.64 (s, C_6H_6), 4.36 (d, J(PH) = 5.9 Hz, C=CHPh), 2.36 (s, C_5Me_5), 1.47 (d, J(PH) = 9.4 Hz, PCH_3), 1.20 and 1.04 (both d, J(PH) = 13.8 Hz, $PCCH_3$).

Preparation of the *Z* Isomer of [(C_6H_6)(P^iPr_3)$\overline{OsC(=CHPh)NC(Ph)O}$] (*Z*-50). A solution of **30** (150 mg, 0.28 mmol) in 10 mL of ether was treated at -78 °C with benzoyl azide (41.6 mg, 0.28 mmol). After the solution was slowly warmed to room temperature, the solvent was removed and the residue was extracted with pentane. The pentane solution was filtered and then brought to dryness in vacuo. The residue was dissolved in 3 mL of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V). With benzene, a brown fraction was eluted. It was concentrated to ca. 2 mL, and then pentane (10 mL) was added. After the solution was cooled to -78 °C, yellow-brown crystals were obtained, yield 142 mg (78%). Mp: 102 °C dec. Anal. Calcd for $C_{30}H_{38}NOOsP$: C, 55.45; H, 5.89; N, 2.16; Os, 29.27. Found: C, 55.08; H, 6.06; N, 1.84; Os, 29.55. MS (70 eV): m/z 651 (39, M^+), 532 (15, M^+ - OCNPh), 530 (17, M^+ - $PhCONH_2$). IR (KBr): ν(C=C) 1582, ν(C=N) 1535 cm^{-1}. ^1H NMR (C_6D_6): δ 7.81 (m, C_6H_5), 4.95 (s, C_6H_6), 1.89 (m, PCHCH_3), 0.91 (dd, J(PH) = 12.6 Hz, J(HH) = 6.2 Hz, $PCHCH_3$), signal of =CHPh proton probably masked by signal of C_6H_5. ^{31}P NMR (C_6D_6): δ 18.9 (s).

Table II. Atomic Positional Parameters (×10⁴) and Isotropic Thermal Parameters ($pm^2 \times 10^{-1}$) for 21

	x	y	z	U^a
Os	3683 (1)	9848 (1)	8241 (1)	40 (1)
I	3481 (1)	9059 (1)	9629 (1)	64 (1)
P	2592 (1)	10298 (1)	7427 (1)	60 (1)
C(1)	3847 (3)	10920 (4)	9078 (4)	45 (2)
C(2)	4094 (3)	11648 (4)	9035 (4)	52 (3)
C(3)	4287 (3)	12338 (4)	9736 (4)	47 (3)
C(4)	4184 (3)	12312 (5)	10530 (5)	58 (3)
C(5)	4398 (4)	12949 (6)	11187 (6)	73 (4)
C(6)	4703 (4)	13632 (6)	11066 (7)	90 (5)
C(7)	4808 (4)	13679 (6)	10288 (8)	89 (5)
C(8)	4599 (4)	13035 (5)	9632 (6)	72 (4)
C(9)	4673 (4)	9318 (8)	8782 (6)	88 (5)
C(10)	4198 (6)	8678 (6)	8239 (9)	104 (7)
C(11)	3750 (5)	8812 (6)	7296 (7)	82 (5)
C(12)	3732 (4)	9592 (6)	6911 (5)	69 (4)
C(13)	4188 (4)	10207 (5)	7425 (7)	76 (5)
C(14)	4653 (4)	10038 (5)	8378 (6)	76 (4)
C(15)	2009 (4)	9491 (7)	6705 (6)	87 (4)
C(16)	2232 (4)	10653 (6)	8190 (9)	112 (6)
C(17)	2438 (5)	11124 (11)	6542 (12)	242 (11)
C(18)	2055 (5)	8712 (7)	7262 (8)	107 (6)
C(19)	2058 (6)	9227 (11)	5823 (8)	164 (9)
C(20)	1514 (5)	10466 (10)	7851 (13)	184 (11)
C(21)	2375 (5)	11524 (8)	8541 (12)	179 (10)
C(22)	2832 (6)	11635 (7)	6462 (8)	118 (7)
C(23)	1722 (6)	11359 (11)	5965 (15)	307 (14)
C(24)	0	919 (11)	2500	132 (13)
C(25)	488 (7)	2213 (13)	3121 (13)	164 (13)
C(26)	496 (7)	1320 (12)	3137 (10)	160 (10)
C(27)	0	2558 (12)	2500	154 (19)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Preparation of the *E* Isomer of [(C_6H_6)(P^iPr_3)$\overline{OsC(=CHPh)NC(Ph)O}$] (*E*-50). A solution of *Z*-**50** (100 mg, 0.16 mmol) in 10 mL of benzene was stirred for 2 h at 60 °C. After cooling of the solution to room temperature, the solvent was removed and the residue was dissolved in 30 mL of pentane. The pentane solution was filtered, and the filtrate was concentrated to ca. 5 mL in vacuo. After stepwise cooling of the solution first to -20 °C and then to -78 °C, yellow-brown crystals were isolated, yield 81 mg (83%). Mp: 109 °C dec. Anal. Calcd for $C_{30}H_{38}NOOsP$: C, 55.45; H, 5.89; N, 2.16; Os, 29.27. Found: C, 55.55; H, 6.00; N, 1.77; Os, 29.50. MS (70 eV): m/z 651 (41, M^+), 532 (23, M^+ - OCNPh), 530 (26, M^+ - $PhCONH_2$). IR (KBr): ν(C=C) 1580, ν(C=N) 1505 cm^{-1}. ^1H NMR (C_6D_6): δ 7.89 (m, C_6H_5), 6.12 (d, J(PH) = 2.5 Hz, =CHPh), 4.86 (s, C_6H_6), 2.01 (m, PCHCH_3), 0.91 (dd, J(PH) = 12.7 Hz, J(HH) = 6.7 Hz, $PCHCH_3$). ^{13}C NMR (C_6D_6): δ 179.50 (s, C=N), 143.03 (s, C=CHPh), 135.21 (s, C=CHPh), 129.82, 129.10, 128.56, 128.45, 128.39, 128.22, 127.09, 127.04, 123.19 (all s, C_6H_5), 79.17 (s, C_6H_6), 26.18 (d, J(PC) = 24.1 Hz, $PCHCH_3$), 19.98 and 19.80 (both s, $PCHCH_3$). ^{31}P NMR (C_6D_6): δ 2.53 (s).

X-ray Structure Analysis of 21. Brownish yellow crystals of **21** were obtained from benzene. A needlelike crystal (0.15 × 0.2 × 1.35 mm) was mounted on a Syntex P3 automatic four-circle diffractometer. Mo Kα radiation (λ = 0.71069 Å, graphite monochromator) was used for all measurements. Centering and refinement of 15 reflections resulted in the following unit-cell parameters: a = 23.323 (6), b = 15.697 (7), c = 15.832 (5) Å; β = 117.42 (2)°; V = 2563.5 Å^3. By systematic absences monoclinic space group $C2/c$ (No. 15) was established; d(calcd) = 1.671 g/cm^3 (Z = 8); the linear absorption coefficient was 61.12 cm^{-1}. Diffraction intensities were measured in an ω-scan mode (scan range

1°); the scan rate varied as a function of maximum peak intensity from 0.5 to 29.3°/min. A total of 4694 independent reflections were collected ($2\theta_{max}$ = 55°) of which 4679 with $F > 3\sigma(F)$ were used for the refinement. The structure was solved by the Patterson method and refined by anisotropic full-matrix least squares. The hydrogen positions were calculated and considered isotropically. Final R = 0.035 and R_w = 0.036. The final atomic positional parameters of the non-hydrogen atoms are given in Table II. The compound crystallizes with one molecule of benzene in the asymmetric unit. The carbon atoms C24 and C27 lie on a 2-fold axis that generate atoms C24a and C25a.

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Supplementary Material Available: A table of structure factors for 21 (28 pages). Ordering information is given on any current masthead page.

Synthesis, Reactivity, and Characterization of the First Donor-Stabilized Silylene Complexes of Osmium *meso*-Tetra-*p*-tolylporphyrin (TTP)Os=SiR_2·THF (R = Me, Et, ^{i}Pr) and the Molecular Structure of (TTP)Os=$SiEt_2$·2THF

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The preparation and characterization of the first donor-stabilized silylene complexes of osmium *meso*-tetra-*p*-tolylporphyrin are described. The silylene complex (TTP)Os=$SiMe_2$·THF (1·THF) is prepared by the reaction of $[Os(TTP)]_2$ with hexamethylsilacyclopropane. Treating $K_2[Os(TTP)]$ with Cl_2SiR_2 also generates the silylene complexes (TTP)Os=SiR_2·THF [R = Me (1·THF), Et (2·THF), ^{i}Pr (3·THF)]. ^{1}H NMR spectroscopy indicates that, in solution, one molecule of THF is coordinated to the silicon in all of these complexes. This has been verified by 2D-NOESY experiments. In 2·THF, the methylene protons are diastereotopic, indicating that the silicon is pyramidalized. Addition of 1 equiv of pyridine to 1·THF or 2·THF replaces the THF on silicon with pyridine. Coordination of pyridine to silicon was also confirmed by a 2D-NOESY experiment. The structure of 2·THF was determined by a single-crystal X-ray diffraction experiment. The diethyl complex 2·2THF crystallizes with two additional THF molecules as solvates in the monoclinic space group $P2_1/c$ with a = 21.649 (5) Å, b = 13.829 (3) Å, c = 19.526 (3) Å, β = 98.08 (2)°, V = 5788 (4) Å^3, Z = 4, R = 5.0%, and R_w = 5.7%. The Os–Si distance (2.325 (8) Å) is the shortest observed to date. Other metrical parameters of this complex are discussed.

Introduction

In contrast to the well-established chemistry of terminal transition-metal carbene complexes,[2] much less is known for the heavier group 14 analogues, terminal silylene complexes. In the latter case, preparation and investigation of this type of compound has been achieved solely with the use of organometallic complexes. For example, one of the first reported syntheses employed Collman's reagent, $Na_2Fe(CO)_4$, as a metal source in reaction with $(^tBuO)_2SiCl_2$ to yield $(CO)_4Fe$=$Si(O^tBu)_2$·L (L = HMPT, THF).[3] Subsequently, Tilley demonstrated that electrophilic abstraction of a silicon-based group from a ruthenium silyl complex can produce cationic base-stabilized complexes such as $[Cp^*(PMe_3)_2Ru$=$SiPh_2$·$NCCH_3]^+$.[4] More recently, Ogino has obtained a donor-stabilized bis(silylene) complex by photolysis of Cp^*-$(CO)_2FeSiMe_2SiMe(OMe)_2$.[5] Only nine examples of silylene complexes have been structurally characterized by X-ray diffraction, and in all cases, coordination of a donor molecule to silicon is observed.[3-5,6,7] Thus, a particularly significant development is Tilley's report of the first iso-

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