Synthesis, Molecular Structure, and Reactivity of Neutral and Cationic Areneosmium(II) Complexes with Diarylcarbenes as Ligands§

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While the dinuclear compounds [(η^6-mes)Os{κ^1-OC(O)CF_3}(μ-Cl)]$_2$ (**2**) and [(η^6-mes)Os{κ^1-OS(O)$_2$$CF_3$}($\mu$-Cl)]$_2$ (**3**), prepared from [(η^6-mes)OsCl(η^3-C_3H_5)] (**1**) and CF_3CO_2H or CF_3SO_3H by elimination of propene, are not suitable precursors for the synthesis of osmium carbenes, the bis(trifluoroacetato) derivatives [(η^6-arene)Os{κ^1-OC(O)CF_3}(κ^2-O_2CCF_3)] (**4**, **9**, **10**) are useful starting materials. They react with diaryldiazomethanes R_2CN_2 to give the half-sandwich-type complexes [(η^6-arene)Os{κ^1-OC(O)CF_3}$_2$(=CR_2)] (**11**−**17**) in good to excellent yields. The bis(tosylato)osmium(II) compounds [(η^6-arene)Os{κ^1-OS(O)$_2$R}{κ^2-O_2S(O)R}] (**20**, **21**; R = *p*-$C_6H_4CH_3$) behave differently and upon treatment with Ph_2CN_2 and $PhCHN_2$ afford tetraphenylethene and a mixture of (*E*)- and (*Z*)-stilbene. The reaction of **12**−**15** and **17** with either Me_3SiX or NH_4X (X = Cl, Br, I) leads to the replacement of the trifluoroacetato ligands and the formation of the corresponding carbene complexes [(η^6-arene)OsX_2(=CR_2)] (**22**−**31**) in 67−91% yield. An exchange of trifluoroacetate for chloride or bromide by using HCl or HBr is also possible. Treatment of [(η^6-mes)$OsCl_2$(=CPh_2)] (**28**) with M(acac-[F_n]) (M = Na, Tl; *n* = 0, 3, or 6) affords the chelate compounds [(η^6-mes)OsCl(κ^2-acac-[F_n])] (**33**−**35**) via elimination of the carbene ligand. Compounds **33**−**35** are also accessible from [(η^6-mes)-$OsCl_2$]$_2$ (**19**) and Hacac/NEt_3 or Na(acac-[F_n]) (*n* = 3 or 6), respectively. While **14** (arene = mes; R = Ph) and **28** react with C_6H_5MgBr and CH_3MgI only by displacement of trifluoroacetate or chloride for bromide or iodide, the reaction of **14** with CH_2=CHMgBr gives the η^3-allyl complex [(η^6-mes)OsBr(η^3-CH_2CHCPh_2)] (**36**). A C−C coupling also takes place upon treatment of **14** with CH_2=CHOEt, resulting in the formation of the metallacyclic compound [(η^6-mes)Os{κ^2(*C*,*O*)-Ph_2*C*CH=CH*O*Et}{κ^1-OC(O)CF_3}] (**38**). The bis(trifluoroacetato) derivatives **14**, **15**, and **17** react in acetone with water to afford the diaryl(carbonyl)-osmium(II) complexes [(η^6-mes)OsR_2(CO)] (**39**−**41**). On the basis of a labeling experiment, a mechanism for this unusual C−C cleavage reaction is proposed. The reaction of the dichloro compounds **28** and **29** with PPh_3 in the presence of $AgPF_6$ gives the cationic carbene complexes [(η^6-mes)OsCl(PPh_3)(=CR_2)]PF_6 (**45**, **46**) in nearly quantitative yields. The molecular structures of **2**, **15**, **28**, **35**, and **46** were determined crystallographically.

Introduction

In the course of our investigations on the reactivity of carbenemetal complexes, in which a non-Fischer-type carbene ligand is coordinated to an electron-rich metal center, we recently reported that diarylcarbeneruthenium(II) compounds of the general composition [(η^5-C_5H_5)RuX(=CRR′)(PPh_3)] (R = R′ = aryl; X = Cl, acetate) can easily be obtained from the acetato derivative [(η^5-C_5H_5)Ru(κ^2-O_2CCH_3)(PPh_3)] as the precursor.[1] This complex reacts with diaryldiazomethane in toluene at room temperature via elimination of N_2 to give the compounds [(η^5-C_5H_5)Ru{κ^1-OC(O)CH_3}(=CRR′)(PPh_3)], which upon treatment with [Et_3NH]Cl are converted to the more stable chloro derivatives [(η^5-C_5H_5)RuCl(=CRR′)(PPh_3)]. As far as the reactivity of these complexes is concerned, the most interesting facet is that they react with Grignard reagents or organolithium compounds not only by substitution of chloride but subsequently also by C−C coupling of the carbene ligand with a methyl, phenyl, or vinyl moiety to generate an olefin or an allyl group coordinated to ruthenium(II).[1,2]

By taking into consideration that earlier attempts to prepare half-sandwich-type carbeneosmium(II) complexes [(η^6-arene)OsX_2(=CRR′)] (X = Cl, I) from [(η^6-arene)OsX_2]$_n$ and diaryldiazomethanes failed,[3] we decided to use instead of the dichlorides or diiodides the

§ Dedicated to Professor Robert H. Grubbs on the occasion of his 60th birthday.

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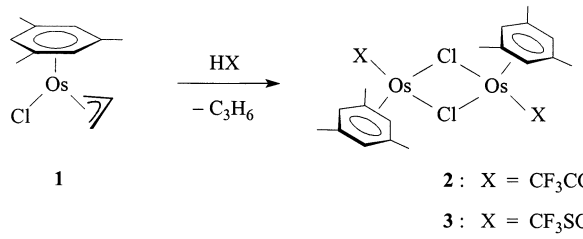
Scheme 1



1

2: X = CF_3CO_2

3: X = CF_3SO_3

corresponding bis(trifluoroacetates) [(η^6-arene)Os{κ^1-OC(O)CF_3}{κ^2-O_2CCF_3}] as the starting materials. We found that this was the method of choice. In the present paper we report the synthesis of a series of mononuclear areneosmium(II) complexes with an osmium−carbene bond and show that, although the reactivity of these compounds is less pronounced than that of their ruthenium counterparts, under particular conditions they also undergo C−C coupling reactions. Moreover, we illustrate that from the neutral compounds [(η^6-arene)-OsX_2(=CRR′)] related cationic species can be obtained and that besides the bis(trifluoroacetates) also areneosmium(II) complexes with OsCl{κ^1-OC(O)CF_3}, OsCl-{κ^1-$OS(O)_2CF_3$}, and OsCl{κ^2-acac} as building blocks are accessible. Some preliminary results of these studies have already been communicated.[4]

Results and Discussion

1. Preparation of Neutral Half-Sandwich-Type Complexes [(η^6-arene)Os{κ^1-OC(O)CF_3}$_2$(=CR_2)]. On the basis of our experience with the synthesis of the ruthenium compounds [(η^5-C_5H_5)RuX(=CRR′)(PPh_3)], we initially considered the mono(trifluoroacetato) and mono(triflato) complexes **2** and **3** as suitable precursors for the wanted osmium carbenes. Compounds **2** and **3** were prepared from the η^3-allylosmium derivative **1**,[5] which reacts with equimolar amounts of CF_3CO_2H or CF_3SO_3H by elimination of propene to give the products in nearly quantitative yields (Scheme 1). The X-ray crystal structure analysis of **2** reveals that in the crystal the compound is a centrosymmetric dimer with a pseudo-octahedral coordination sphere around each metal center (Figure 1). The Os−C and Os−Cl bond lengths as well as the Os−Cl−Os and Cl−Os−Cl bond angles are quite similar to those of [(η^6-cym)OsCl(μ-Cl)]$_2$[6] and thus deserve no further comment.

Quite surprisingly, the NMR spectra of the trifluoroacetato compound **2** indicate that the molecular structure found in the crystal is not maintained in solution. The ^{1}H NMR spectrum of **2** (in $CDCl_3$) displays four sets of signals for the CH and CH_3 protons of the mesitylene ring, which could be due to the presence of the three equilibrating species shown in Scheme 2. Both the observation of five resonances for the ^{19}F nuclei of the CF_3CO_2 groups in the ^{19}F NMR spectrum of **2** and the conductivity Λ = 63 cm^2 Ω^{-1} mol^{-1} (measured in CD_3-NO_2) support this proposal. It should be mentioned that one of us already reported the isolation of the ionic ruthenium complex [(η^6-C_6Me_6)$_2$$Ru_2$($\mu$-Cl)$_2$($\mu$-$O_2CCF_3$)]-

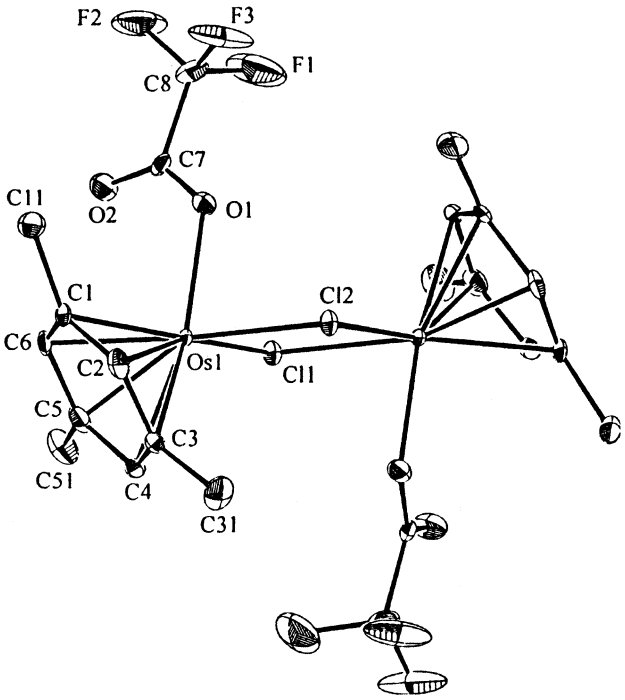
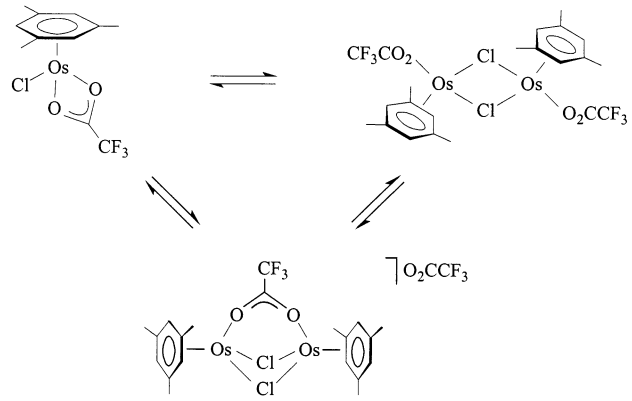


Figure 1. Molecular diagram of compound **2**. Selected bond distances (Å) and angles (deg): Os1−Cl1 2.448(2), Os1−Cl2 2.430(2), Os1−O1 2.120(7), Os1−C1 2.170(8), Os1−C2 2.156(8), Os1−C3 2.174(8), Os1−C4 2.161(9), Os1−C5 2.184(9); Os1−C6 2.161(8); Cl1−Os1−Cl2 80.40-(8), Cl1−Os1−O1 82.1(2), Cl2−Os1−O1 81.6(2), Os1−Cl1−Os2 99.1(1), Os1−Cl2−Os2 100.1(1).

Scheme 2



(CF_3CO_2), which seems to be preferred compared to the neutral species [(η^6-C_6Me_6)Ru{κ^1-OC(O)CF_3}(μ-Cl)]$_2$.[7] In contrast to **2**, the ^{1}H and ^{19}F NMR spectra of **3** are in complete agreement with the existence of a nonionic dimer in solution and give no hint for a similar dissociation as depicted in Scheme 2 for the trifluoroacetato derivative.

While attempts to use either **2** or **3** as precursor for the preparation of carbeneosmium(II) compounds [(η^6-mes)OsCl(X)(=CRR′)] failed, the bis(trifluoroacetato) complexes **4**, **9**, and **10** proved to be suitable starting materials. In exploratory experiments it was first shown that upon treatment of the mesitylene compound **4**[8] with

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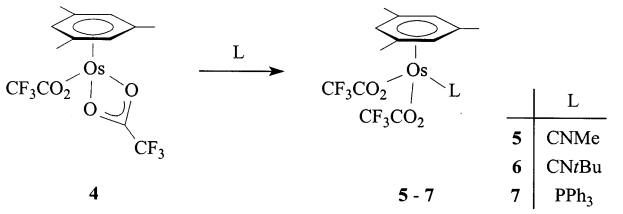
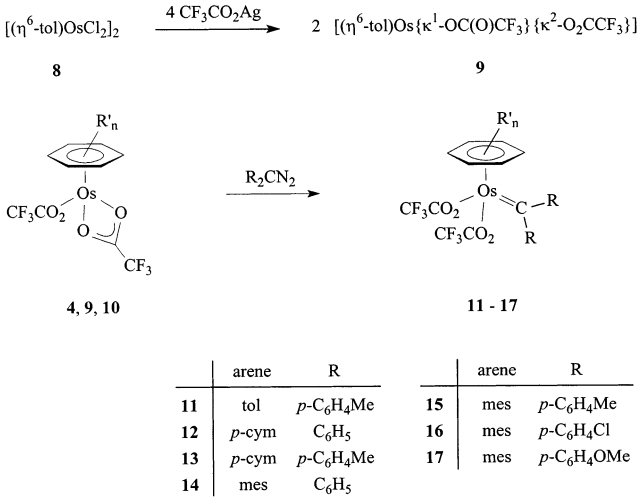
Scheme 3



	L
5	CNMe
6	CN*t*Bu
7	PPh_3

Scheme 4[a]



	arene	R
11	tol	*p*-C_6H_4Me
12	*p*-cym	C_6H_5
13	*p*-cym	*p*-C_6H_4Me
14	mes	C_6H_5

	arene	R
15	mes	*p*-C_6H_4Me
16	mes	*p*-C_6H_4Cl
17	mes	*p*-C_6H_4OMe

[a] **10**: arene = *p*-cym.

CNMe, CN*t*Bu, or PPh_3, an opening of the Os−(κ^2-O_2CCF_3) chelate ring takes place and the mononuclear isocyanide and phosphine complexes **5**−**7** are formed in 88−95% yield (Scheme 3). The IR and ^{19}F NMR spectroscopic data of **5**−**7** confirm that the CF_3CO_2 ligands are coordinated in a monodentate fashion and that from a structural point of view **5**−**7** are near relatives of the well-known dichloro derivatives [(η^6-mes)$OsCl_2$(L)].[9]

The diarylcarbeneosmium(II) compounds **11**−**17** were obtained under similar conditions as found for **5**−**7** (Scheme 4). Treatment of the starting materials **4**, **9**, and **10** (of which **9** was formally unknown and prepared from **8** and 4 equiv of CF_3CO_2Ag) in benzene with a solution of the corresponding diaryldiazomethane in the same solvent led to a rapid evolution of gas (N_2), and after evaporation of the solvent the complexes **11**−**17** were isolated as olive-green or red-brown, only moderately air-sensitive solids in good to excellent yields. Only in the case of **17** was it necessary to work in CH_2Cl_2 at low temperature because otherwise the formation of the carbene compound was accompanied by that of unknown side products. The most characteristic spectroscopic feature of **11**−**17** is the resonance of the carbene carbon atom in the ^{13}C NMR spectra at δ 300−310, which is considerably shifted to lower field compared with the Fischer-type carbene complex [(η^6-mes)$OsPh_2$-{=C(NHMe)Ph}] (δ 220).[10a] For the ^{13}C nuclei of the C-bonded aryl groups of **11**−**17** only a single set of signals is observed, indicating that at least at room temperature the rotation around the Os−C(carbene) bond is not hindered on the NMR time scale.

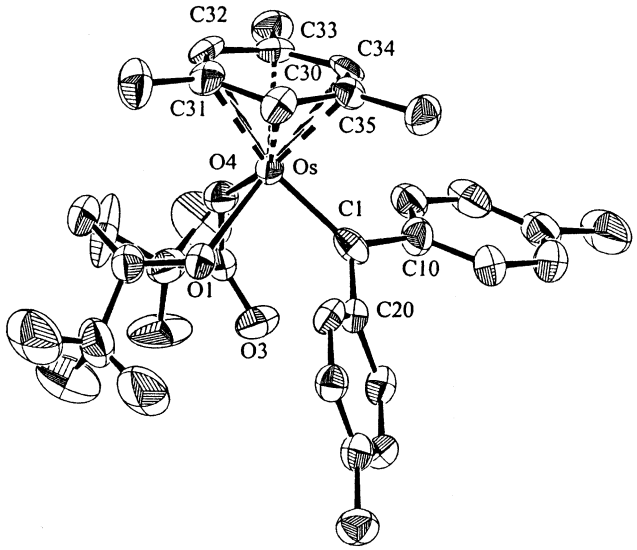


Figure 2. Molecular diagram of compound **15**. Selected bond distances (Å) and angles (deg): Os−C1 1.957(7), Os−O1 2.108(4), Os−O4 2.096(4), Os−C30 2.197(6), Os−C31 2.328(6), Os−C32 2.342(6), Os−C33 2.207(6), Os−C34 2.214(5), Os−C35 2.265(5); C1−Os−O1 85.0(2), C1−Os−O4 95.1(2), O1−Os−O4 81.8(2), Os−C1−C10 121.6(5), Os−C1−C20 123.9(5), C10−C1−C20 114.5(6).

The X-ray crystal structure analysis of **15** (Figure 2) confirms the anticipated piano-stool configuration of the molecule.[4] The Os−C1 distance of 1.957(7) Å is almost identical to that in the five-coordinate osmium(0) compound [OsCl(=CF_2)(NO)(PPh_3)$_2$] (1.967(4) Å)[11] and in the six-coordinate osmium(II) complexes [OsHCl(=CHR)-(CO)(P*i*Pr_3)$_2$] (R = CO_2Et, 1.949(2) Å; R = $SiMe_3$, 1.965-(5) Å) and [$OsCl_2$(=CHR)(CO)(PR'_3)$_2$] (R = Ph, R′ = *i*Pr, 1.95(2) Å; R = 2-naphthyl, R′ = Ph, 1.930(7) Å).[12,13] The Os−C1 distance is, however, slightly shorter than in the above-mentioned half-sandwich-type molecule [(η^6-mes)-$OsPh_2$-{=C(NHMe)Ph}] (1.992(5) Å) with a substituted aminocarbene ligand.[10] The two bond angles C1−Os−O1 and C1−Os−O4 of **15** differ by about 10°, which is probably due to steric hindrance between one of the tolyl moieties and the mesitylene unit. The sum of the bond angles around C1 amounts to 359°, which is in agreement with the sp^2-hybridization of the carbene carbon atom. There is no interaction between one of the oxygen atoms of the CF_3CO_2 groups with the carbon atom C1, as found in a related η^5-cyclopentadienyl ruthenium-(II) complex.[14] The two rings containing the carbon atoms C30 to C35 and C10 to C15 are nearly parallel to each other, the dihedral angle between the two planes being 10.5(2)°.

In contrast to [(η^5-C_5H_5)Ru(κ^2-O_2CCH_3)(PPh_3)], which reacts not only with Ph_2CN_2 but also with phenyldiazo-

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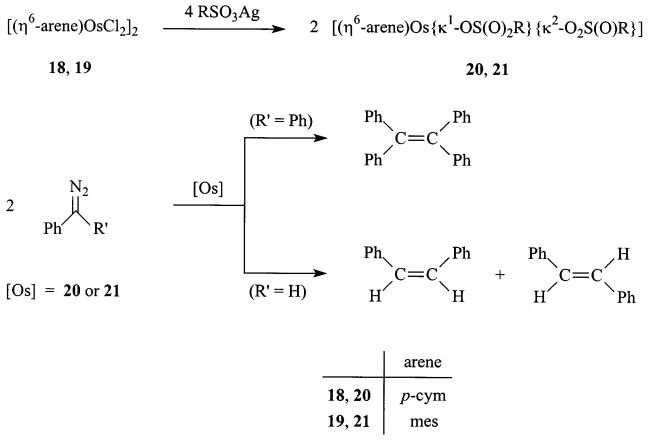
Scheme 5[a]



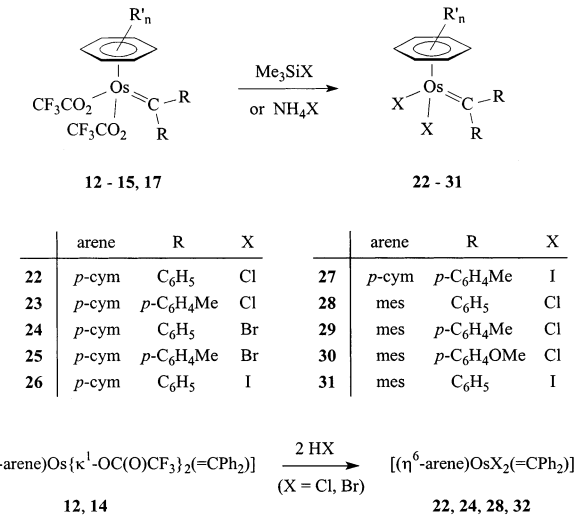
[a] R = *p*-C_6H_4Me.

methane to give the corresponding carbene complex [(η^5-C_5H_5)Ru{κ^1-OC(O)CH_3}(=CHPh)(PPh_3)],[2] the reaction of **4** with $PhCHN_2$ affords besides N_2 only (*Z*)-stilbene as the product. Even at low temperatures, no other osmium-containing species other than the starting material **4** (of which ca. 90% was reisolated) could be detected. Due to the selective formation of the *cis* isomer of stilbene, we assume that initially an Os(=CHPh) intermediate is generated, which presumably reacts with a second molecule of $PhCHN_2$ to give the olefin.

Taking into consideration that in half-sandwich-type transition metal compounds the coordinating abilities of the $CF_3CO_2^-$ and *p*-$CH_3C_6H_4SO_3^-$ anions are quite similar, we assumed that like the bis(trifluoroacetato) complexes **4** and **10** also the bis(tosylato) counterparts **20** and **21** could be suitable precursors for the synthesis of osmium(II) carbenes. The preparation of **20** and **21** proceeded analogously to that of **4** and **10** and gave, by using 4 equiv of silver tosylate for 1 equiv of the dimers **18** or **19**, the wanted products in good yields (Scheme 5). Both the elemental analyses and the ^{1}H NMR spectra confirmed that the isolated solids contained water molecules, which are probably necessary for the formation of the crystal lattices. The ^{1}H NMR spectra of **20** and **21** display both at 295 and 243 K only one set of signals for the C_6H_4 and CH_3 protons of the tosylate units, indicating that a rapid change between the κ^1 and the κ^2 bonding mode of the anionic ligands occurs. In contrast to **4** and **10**, the tosylato analogues **20** and **21** do not react with Ph_2CN_2 by generating a compound with an Os=CPh_2 bond but only gave tetraphenylethene. Similarly, upon treatment of **20** or **21** with $PhCHN_2$ a 1:1 mixture of (*E*)- and (*Z*)-stilbene is formed, independent of whether the reactions are carried out at room temperature or at −78 °C. In both cases, the starting material could be reisolated nearly quantitatively.

2. Ligand Replacement Reactions of the Carbene Complexes [(η^6-arene)OsX_2(=CR_2)]. As was already mentioned, the dichloro analogues of **12**−**15** are not accessible from the corresponding dimers **18**, **19**, and diphenyl- or di(*p*-tolyl)diazomethane.[3] However, treatment of **12**−**15** and also of **17** with a 3-fold excess of Me_3SiCl in dichloromethane at −78 °C affords, after warming of the solution to room temperature, evaporation of the solvent, and recrystallization of the residue from toluene/hexane, the dichloroosmium(II) compounds **22**, **23**, and **28**−**30** in 67−87% yield (Scheme 6). On a similar route, the dibromo derivatives **24** and **25** are obtained from **12**, **13**, and Me_3SiBr and like the dichloro counterparts isolated as brown, almost air-stable solids in excellent yields. An alternative preparative route to **22**, **24**, **28**, and **32** consists of the reaction of the bis(trifluoroacetates) and HCl or HBr, respectively, in this case benzene being the preferred solvent. Regarding the spectroscopic data of **22**−**25**, **28**−**30**, and **32**, a noteworthy aspect is that in the ^{13}C NMR spectra the carbene carbon resonance appears at δ ca. 300 and thus at slightly higher field compared with the analogous bis(trifluoroacetato) derivatives.

Scheme 6[a]



	arene	R	X
22	*p*-cym	C_6H_5	Cl
23	*p*-cym	*p*-C_6H_4Me	Cl
24	*p*-cym	C_6H_5	Br
25	*p*-cym	*p*-C_6H_4Me	Br
26	*p*-cym	C_6H_5	I
27	*p*-cym	*p*-C_6H_4Me	I
28	mes	C_6H_5	Cl
29	mes	*p*-C_6H_4Me	Cl
30	mes	*p*-C_6H_4OMe	Cl
31	mes	C_6H_5	I

[a] **32**: [(η^6-mes)$OsBr_2$(=CPh_2)].

The synthesis of the diiodo complex **31** has been achieved from **14** and Me_3SiI. For the preparation of the related compounds **26** and **27** instead of Me_3SiI even NH_4I could be used as an iodide source, the driving force probably being the well-known strength of the Os−I bond.[15] Attempts to substitute the CF_3CO_2 ligands in **12** or **14** by fluoride failed, independent of whether NaF, CsF, AgF, or [NBu_4]F was used as the substrate.

The molecular structure of the dichloro compound **28** is shown in Figure 3. It crystallizes in the chiral space group *C*2, and since the single crystals were grown from CH_2Cl_2/pentane, it contains one-half molecule of dichloromethane in the asymmetric unit. Due to the presence of H−Cl−H bridges between the chloro ligand Cl2 and the hydrogen atoms of CH_2Cl_2 and the hydrogen atom H14 linked to the phenyl carbon atom C14 of a neighbored molecule, a network between the half-sandwich-type complex **28** and the solvent is built up in the crystal lattice, which is illustrated in Figure 4. The structure of each single molecule of **28** is similar to that of **15** (see Figure 2), the bond length Os−C1 being nearly identical in both compounds. The difference between the bond angles C1−Os−Cl1 and C1−Os−Cl2 in **28** (ca. 6°) is less than the difference between the bond angles C1−Os−O1 and C1−Os−O2 in the bis(trifluoroacetato) analogue **15** (ca. 10°) probably due to the different size of the anionic ligands.

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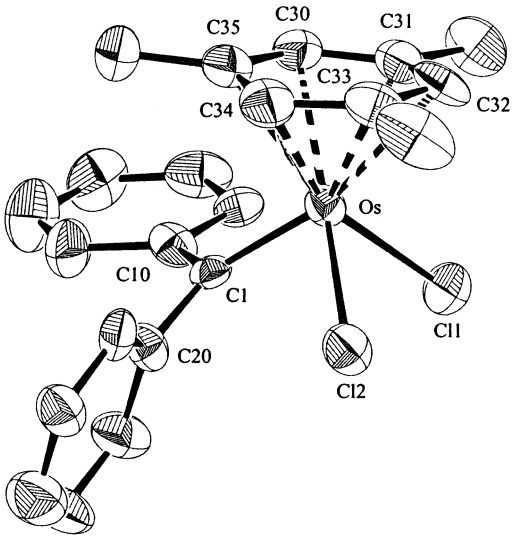


Figure 3. Molecular diagram of compound **28**. Selected bond distances (Å) and angles (deg): Os−C1 1.947(5), Os−Cl1 2.399(2), Os−Cl2 2.387(1), Os−C30 2.222(9), Os−C31 2.221(6), Os−C32 2.346(5), Os−C33 2.321(6), Os−C34 2.202(7), Os−C35 2.274(7); C1−Os−Cl1 95.2(3), C1−Os−Cl2 89.4(2), Cl1−Os−Cl2 83.61(7), Os−C1−C10 122.7(3), Os−C1−C20 124.2(3), C10−C1−C20 113.1(4).

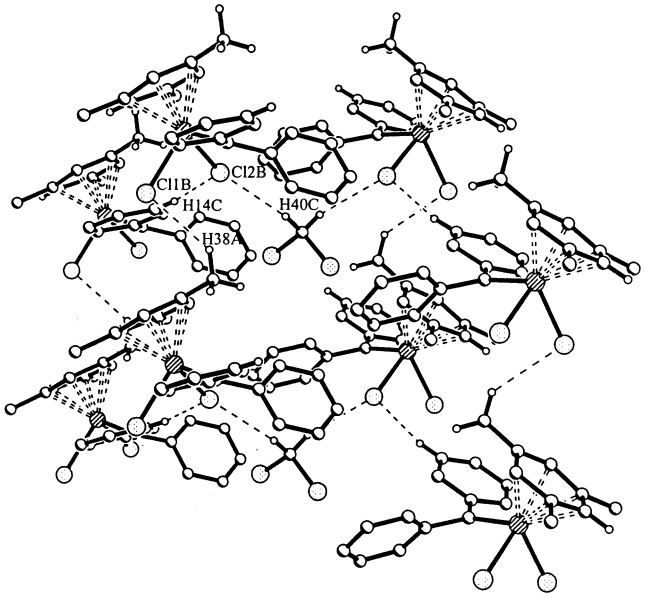


Figure 4. Packing of the molecules of **28** and CH_2Cl_2 in the crystal (XP plot). The dotted lines indicate the bridging bonds between the hydrogen atoms of the solvent molecule and the chloro ligands of the osmium complex. Selected distances (Å): Cl1B−H38A 2.75, Cl2B−H14C 2.60, Cl2B−H40C 2.68.

The reactions of **28** with Tl(acac) and the trifluoro and hexafluoro derivatives Na(acac-[F_3]) and Na(acac-[F_6]) took an unexpected course. While we had anticipated that the chloro ligands of **28** would be substituted by the chelating unit to afford the ionic complexes [(η^6-mes)Os(κ^2-acac-[F_n])(=CPh$_2$)]Cl (n = 0, 3, or 6), instead of the two halides only one of them plus the carbene group is replaced and the neutral compounds **33**−**35** are formed in moderate to good yields. They can be obtained more conveniently (and almost quantitatively) from the dinuclear precursor **19** and Hacac/NEt_3 or Na(acac-[F_n]), respectively (see Scheme 7). Compound **33** was already

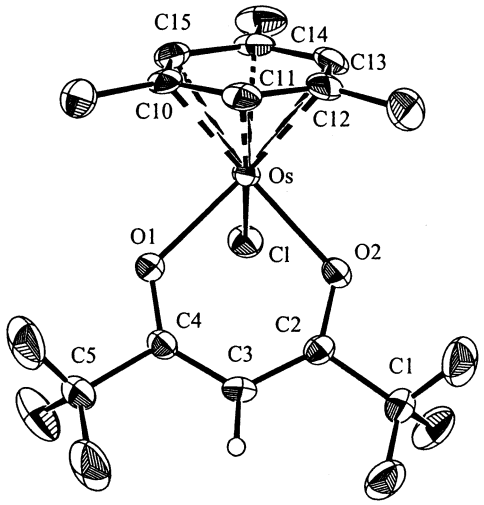
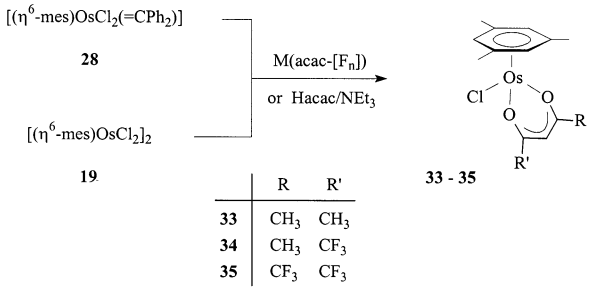


Figure 5. Molecular diagram of compound **35**. Selected bond distances (Å) and angles (deg): Os−Cl 2.405(2), Os−O1 2.111(4), Os−O2 2.105(3), Os−C10 2.198(4), Os−C11 2.201(4), Os−C12 2.200(4), Os−C13 2.191(5), Os−C14 2.194(4), Os−C15 2.185(4); Cl−Os−O1 83.1(1), Cl−Os−O2 82.5(1), O1−Os−O2 86.8(1).

Scheme 7



	R	R'
33	CH_3	CH_3
34	CH_3	CF_3
35	CF_3	CF_3

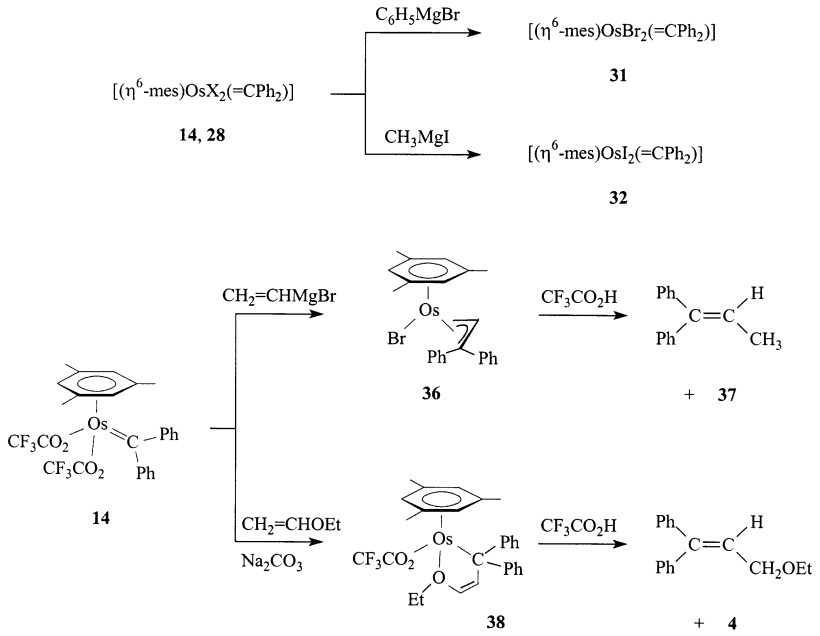
prepared by one of us from **19** and Tl(acac).[16] The Os(acac) complexes **33**−**35** are yellow or red, air-stable, and thermally exceedingly stable solids, for which correct elemental analyses were obtained.

The hexafluoroacetylacetonato complex **35** was also characterized crystallographically. As shown in Figure 5, the coordination sphere around the metal is built up by the six-membered ring, the chloride, and the chelating acac-[F_6] ligand, the bond angles Cl−Os−O1, Cl−Os−O2, and O1−Os−O2 of the three-leg fragment lying between 82.5° and 86.8°. The chelate ring consisting of Os, O1, O2, C2, C3, and C4 is practically planar; the dihedral angle between the two planes [O1,Os,O2] and [O1,C1,C2,C3,C4,C5,O2] is 1,1(2)°.

While upon treatment of **28** with Tl(acac) or Na(acac-[F_n]) one chloride and the carbene are displaced, the reactions of **14** and **28** with C_6H_5MgBr and CH_3MgI lead to the substitution of the two chloro or the two trifluoroacetato ligands by bromide or iodide (Scheme 8). Under various conditions, we never succeeded in generating a product with an Os−C_6H_5 or Os−CH_3 bond. This result is surprising insofar as the reactions of [(η^6-mes)OsCl_2(CNMe)] with either C_6H_5MgBr or RMgI (R = CH_3, C_6H_5) led partly or completely to the replacement of chloride by phenyl or methyl, respectively.[17]

(16) Bennett, M. A.; Mitchell, T. R. B.; Stevens, M. R.; Willis, A. C. *Can. J. Chem*. **2001**, *79*, 655−669.
(17) Werner, H.; Wecker, U.; Schulz, M.; Stahl, S. *Organometallics* **1991**, *10*, 3278−3282.

Scheme 8[a]



[a] **37**: [(η^6-mes)OsBr(κ^2-O_2CCF_3)].

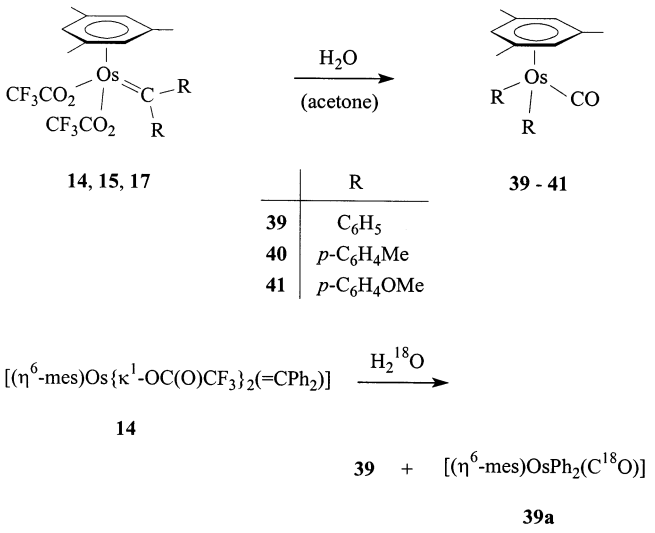
3. C−C Coupling and C−C Cleavage Reactions of Carbeneosmium(II) Complexes. The vinyl Grignard reagent CH_2=CHMgBr behaves differently compared with C_6H_5MgBr. Treatment of a solution of **14** in THF with a solution of CH_2=CHMgBr in the same solvent at low temperature affords, after chromatographic workup and recrystallization from hexane, the (η^3-allyl)osmium(II) complex **36** as a yellow, slightly air-sensitive solid in 61% isolated yield (Scheme 8). We assume that a carbene(η^1-vinyl) metal species is formed as an intermediate, which by intramolecular C−C coupling is transformed to the final product. An alternative pathway, addition of the C-nucleophile to the carbene carbon atom followed by elimination of trifluoroacetate with concomitant η^1/η^3 allyl rearrangement, could equally be considered. Although on the basis of the ^{1}H and ^{13}C NMR data it cannot be decided whether the η^3-CH_2CHCPh_2 ligand of **36** is linked in *exo* or *endo* position to the (η^6-mes)OsBr moiety, there is no doubt that in contrast with the η^5-cyclopentadienylruthenium compounds [(η^6-C_5H_5)Ru(η^3-CH_2CHCR_2)(PPh_3)] (R = *p*-C_6H_4X)[1] only one isomer is present. In analogy with the crystallographically characterized η^3-2-methallyl complex [(η^6-mes)OsCl{η^3-$CH_2C(CH_3)CH_2$}][10b] we believe that the *exo* isomer is thermodynamically preferred. We note that the reaction of **36** with CF_3CO_2H gives besides [(η^6-mes)OsBr(κ^2-O_2CCF_3)] (**37**) the trisubstituted ethene derivative Ph_2C=$CHCH_3$.

A C−C coupling involving the diphenylcarbene ligand of **14** also occurs upon treatment of **14** with ethyl(vinyl)-ether in the presence of Na_2CO_3. Stirring a mixture of **14** and Na_2CO_3 in CH_2=CHOEt as the solvent at room temperature causes a smooth change of color from dark green to brown and finally gives the metallacyclic product **38** as a pale brown solid in 78% yield. The ^{1}H NMR spectrum of **38** displays two doublets at δ 5.88 and 5.28 for the olefinic CH protons of the five-membered ring, the H−H coupling constant of 7.4 Hz being typical for a *Z* configuration of the −CH=CH− unit. The resonances for the corresponding CH carbon atoms appear in the ^{13}C NMR spectrum of **38** at δ 148.1 and 142.8, while the signal for the metal-bonded *C*Ph_2 carbon atom is observed at δ 61.7. Regarding the mechanism of the formation of **38**, it is conceivable that in the initial step a substitution of one carboxylate ligand by CH_2=CHOEt takes place followed by abstraction of a proton from the less electron-rich part of the coordinated olefin with Na_2CO_3. The so-formed η^1- or η^2-bonded vinylic unit could then undergo an intramolecular C−C coupling reaction with the CPh_2 group similar to what probably occurs during the formation of **36**. Although d^6 transition metal centers are not particularly oxophilic, we assume that not only for steric but also for electronic reasons the five-membered OsC_3O ring is preferred compared to an OsC_3 ring or an η^3-allylosmium species containing an OEt substituent. We note that recently Caulton, Eisenstein, and co-workers reported that the coordinatively unsaturated cation $[RuH(CO)(PR_3)_2]^+$ (PR_3 = P*t*Bu_2) reacts with methyl- and ethyl(vinyl)ether to afford β-alkoxyethylruthenium(II) complexes with a Ru−O bond.[18] Treatment of the osmium compound **38** with CF_3CO_2H leads to protolytic cleavage of the Os−C bond and to the generation of the substituted allyl(ethyl)ether Ph_2C=$CHCH_2OEt$ (see Scheme 8).

In the course of experiments aimed to replace one trifluoroacetato ligand of **14**, **15**, or **17** by a solvent molecule and thus to generate a reactive cationic species [(η^6-mes)Os{κ^1-OC(O)CF_3}(S)(=CR_2)]$^+$ (S = solvent), we discovered a C−C cleavage reaction for which, as far as we know, there is no precedence. The bis(trifluoroacetato) complexes **14**, **15**, and **17** react with water in acetone solution to give the diaryl(carbonyl)osmium(II) compounds **39**−**41** (Scheme 9) in good to excellent yields. The diphenyl derivative **39** was already known and had previously been prepared in our laboratory from [(η^6-mes)$OsCl_2$(CO)] and C_6H_5Li.[19] Similarly to **39**,

(18) Huang, D.; Gérard, H.; Clot, E.; Young, V.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1999**, *18*, 5441−5443.

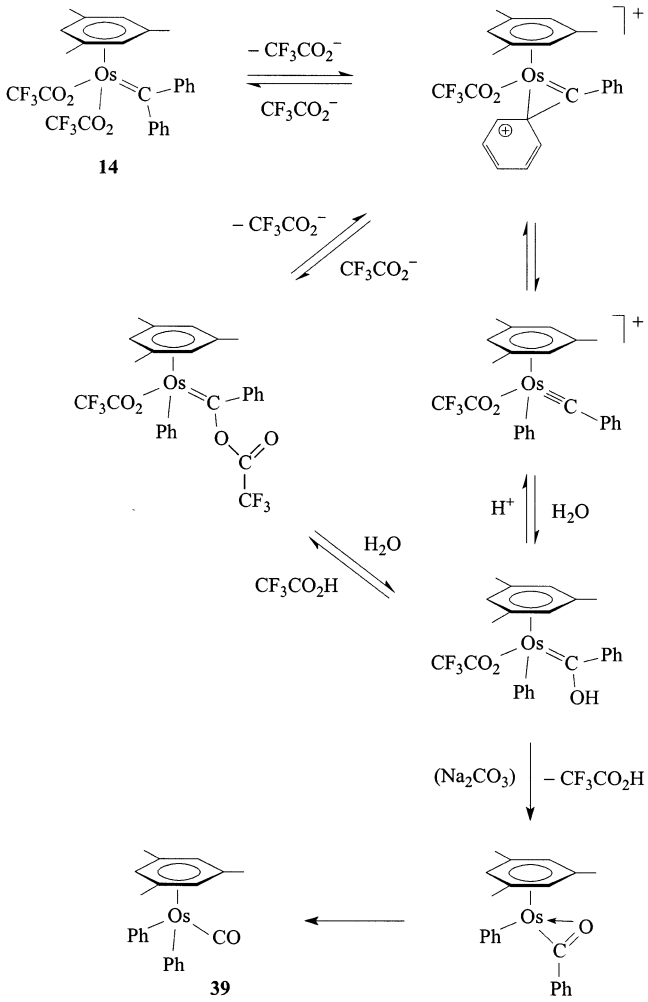
Scheme 9



also the analogous complexes **40** and **41** are yellow solids, which are only moderately air-sensitive and soluble in all common organic solvents. The most typical spectroscopic features are the strong ν(CO) absorption in the IR spectrum at 1924 (**40**) and 1942 cm^{-1} (**41**) and the resonance for the CO carbon atom in the ^{13}C NMR spectrum at δ 184.8 (**40**) and 179.1 (**41**), respectively.

A proposal for the mechanism of the unusual C−C cleavage reaction (exemplified for R = C_6H_5) is shown in Scheme 10. We assume that in the initial step the anticipated dissociation of one of the trifluoroacetate ions occurs followed by an attack of the positively charged metal center on the *ipso*-carbon atom of one phenyl group. The subsequent C−C bond cleavage could lead to a cationic $[Os(C_6H_5)(\equiv CC_6H_5)]^+$ intermediate, the carbyne carbon atom of which is presumably readily attacked by a nucleophile such as water or a trifluoroacetate anion. Due to this attack, a hydroxocarbene intermediate is generated in one or two steps and rearranges, after cleavage of the Os−$OC(O)CF_3$ bond and abstraction of a proton, to a κ^2-bonded benzoylosmium(II) species. Finally, migration of the phenyl group from the Ph*C*(O) carbon to osmium affords the isolated product. Although the formation of a dicationic dinuclear intermediate cannot be excluded, we consider the possibility of an intermolecular transfer of group R from carbon to osmium as less likely. With regard to the postulated cationic intermediate formed in the initial step, we note that a metallacyclopropene structure has also been discussed in the context of the reactivity of related half-sandwich-type rhodium and molydenum systems.[20,21] Moreover, Roper et al. reported[22] that the cationic carbyneruthenium complex $[RuCl(I)(\equiv CPh)(CO)(PPh_3)_2]^+$ reacts with water to give the phenylruthenium(II) derivative $[RuCl(C_6H_5)(CO)_2(PPh_3)_2]$, probably via an analogous series of steps as proposed in Scheme 10.

Scheme 10

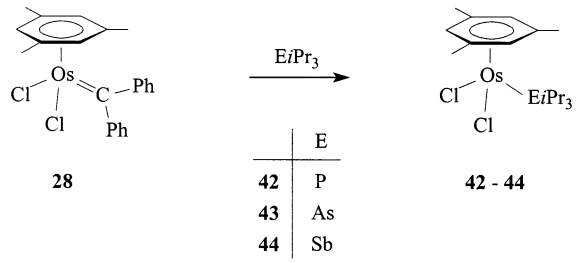


Support for the argument that one of the trifluoroacetate ions is involved in the formation of the CO ligand coordinated to osmium in **39**−**41** stems from a labeling experiment. If the starting material **14** is treated in unlabeled acetone with $H_2{}^{18}O$ and the reaction mixture worked up as described for **39**, the IR spectrum (in CH_2Cl_2) of the residue displays two strong ν(CO) bands at 1946 and 1904 cm^{-1} assigned to **39** and **39a**, respectively. The intensity ratio is approximately 2:1. Since **39a** is not formed exclusively, we assume either that both $H_2{}^{18}O$ and unlabeled $CF_3CO_2^-$ attack the cationic carbyneosmium intermediate in parallel steps or that initially in a fast equilibrium trifluoroacetate reacts with $H_2{}^{18}O$ to give ^{18}O-labeled trifluoroacetate and $H_2{}^{16}O$, the latter being the substrate to form **39** with unlabeled oxygen.

4. Preparation of Cationic Carbeneosmium(II) Complexes. With the aim of further modifying the coordination sphere of osmium(II) in the carbene complexes with $[(\eta^6\text{-arene})Os(=CR_2)]$ as the building block, we also attempted to generate carbeneosmium(II) cations of the general composition $[(\eta^6\text{-mes})Os\{\kappa^1\text{-}OC(O)CF_3\}(L)(=CR_2)]^+$ from the bis(trifluoroacetato) derivatives **14** and **15** and ligands L such as PPh_3, P*i*Pr_3, and As*i*Pr_3 as the precursors. However, under various conditions only decomposition of the osmium compounds occurred. If the dichloro complex **28** is used as the starting material, instead of the substitution of chloride

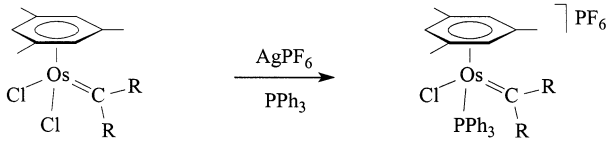
(19) Werner, H.; Stahl, S.; Schulz, M. *Chem. Ber.* **1991**, *124*, 707−712.
(20) Werner, H.; Wolf, J.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* **1983**, *243*, C63−C70.
(21) Feher, F. J.; Green, M.; Rodrigues, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1206−1208.
(22) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121−198.

Scheme 11



	E
42	P
43	As
44	Sb

Scheme 12



	R
45	C_6H_5
46	*p*-C_6H_4Me

by E*i*Pr$_3$ (E = P, As, Sb), the replacement of the carbene by the P-, As-, or Sb-donor takes place (Scheme 11). The so-formed half-sandwich-type osmium(II) compounds **42**−**44** are known and have recently been prepared on a straightforward route from the dimer **19** and E*i*Pr$_3$.[23]

Stable PF_6^- salts of [(η^6-mes)OsCl(L)(=CR_2)]$^+$ cations with L = PPh_3 and R = phenyl or *p*-tolyl were obtained upon teatment of a solution of **28** or **29** in THF with PPh_3 in the presence of $AgPF_6$ at −78 °C (see Scheme 12). After separation of AgCl, evaporation of the solvent and recrystallization of the residue from CH_2Cl_2/hexane dark green solids analyzing as **45** and **46** were isolated in nearly quantitative yields. Conductivity measurements are in agreement with the proposed composition. The ^{13}C NMR spectra of **45** and **46** display a doublet for the carbene carbon atom at δ 292.3 and 291.2, respectively, the signal being shifted ca. 10 ppm upfield compared with the precursors **28** and **29**. It should be mentioned that attempts to prepare the complexes **45** and **46** by an alternative method from [(η^6-mes)-$OsCl_2(PPh_3)$], Ph_2CN_2, and $AgPF_6$ remained unsuccessful.

The molecular structure of the cation of **46** is shown in Figure 6. The X-ray structure analysis of **46** revealed[4] that in the grown single crystal only one enantiomer of the racemate possessing the *R*-configuration at the metal center is present. The cation has the expected piano-stool arrangement with distances between osmium and the carbon atoms of the six-membered ring that are somewhat longer than in the neutral complex **17**. The Os−C(carbene) bond length in both compounds **17** and **46** is nearly identical. Two of the bond angles of the three-legged $OsL^1L^2L^3$ fragment, C1−Os−P1 (93.4-(8)°) and C1−Os−Cl1 (98.1(4)°), are considerably larger than the third one, P1−Os−Cl1 (81.54(9)°), which we assume is due to the steric demand of the carbene ligand.

(23) Weberndörfer, B.; Werner, H. *J. Chem. Soc., Dalton Trans.* **2002**, 1479−1486.

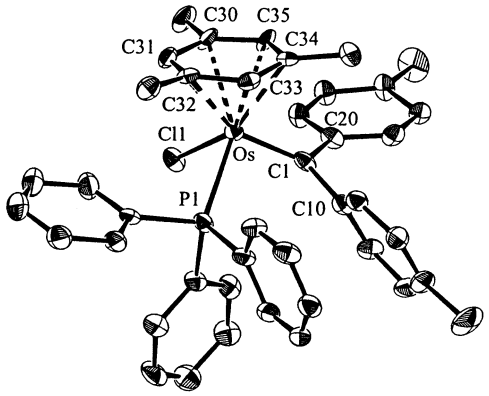


Figure 6. Molecular diagram of compound **45**. Selected bond distances (Å) and angles (deg): Os−C1 1.93(1), Os−Cl1 2.384(2), Os−P1 2.377(2), Os−C30 2.305(9), Os−C31 2.35(1), Os−C32 2.40(1), Os−C33 2.26(1), Os−C34 2.32-(1), Os−C35 2.27(1); C1−Os−Cl1 98.1(4), C1−Os−P1 93.4-(3), Cl1−Os−P1 81.54(9), Os−C1−C10 127.9(8), Os−C1−C20 121.7(8), C10−C1−C20 110(1).

Conclusions

The results presented in this paper illustrate that the bis(trifluoroacetato)osmium(II) compounds [(η^6-arene)-Os{κ^1-OC(O)CF_3}(κ^2-O_2CCF_3)] **(4**, **9**, **10)** are useful starting materials for the preparation of half-sandwich-type complexes containing an Os=CR_2 bond. An unexpected facet is that the related bis(tosylato) compounds [(η^6-arene)Os{κ^1-OS(O)$_2$R}{κ^2-O_2S(O)R}] (**20**, **21**) react with Ph_2CN_2 and $PhCHN_2$ in a different fashion and afford catalytically tetraphenylethene and a mixture of (*E*)- and (*Z*)-stilbene, respectively. Since there is general agreement that tosylate is a better leaving group than trifluoroacetate, we assume that the reactions of **20** and **21** with Ph_2CN_2 and $PhCHN_2$ also give in the initial step a corresponding carbene complex, which, however, seems to be very labile and reacts with a second molecule of the diazoalkane to yield the olefin.

The lability of the Os−OC(O)CF_3 linkages in the bis-(trifluoroacetato) derivatives [(η^6-arene)Os{κ^1-OC(O)-CF_3}$_2$(=CR_2)] opens the gate to prepare dichloro-, dibromo-, and diiodoosmium(II) carbenes [(η^6-arene)-OsX_2(=CR_2)] via ligand exchange using either Me_3SiX or NH_4X (X = Cl, Br, I) and, in some cases, even HCl or HBr as substrates. A remarkable difference has been observed in the reactivity of the η^6-mesitylene complexes [(η^6-mes)OsX_2(=CPh_2)] (X = CF_3CO_2, Cl) toward Grignard reagents. While these compounds react with C_6H_5MgBr and CH_3MgI by replacement of trifluoroacetate or chloride for bromide or iodide, treatment of [(η^6-mes)Os{κ^1-OC(O)CF_3}$_2$(=CPh_2)] (**14**) with CH_2=CHMgBr yields the η^3-allyl complex [(η^6-mes)OsBr(η^3-CH_2CHCPh_2)]. Taking previous results from our laboratory into consideration,[1] we assume that the formation of the η^3-allyl ligand occurs stepwise via an Os(CH=CH_2)(=CPh_2) species as an intermediate. An unusual C−C coupling reaction also takes place upon treatment of **14** with the vinyl ether CH_2=CHOEt, which affords the metallacyclic compound [(η^6-mes)Os{κ^2(*C*,*O*)-Ph_2*C*CH=CH*O*Et}{κ^1-OC(O)CF_3}] in high yield. It is conceivable that equally in this case a carbene(vinyl)-osmium(II) intermediate is involved which after C−C coupling generates an ethoxy-substituted allyl unit that preferentially binds via C and O to the metal.

However, the diarylcarbeneosmium compounds undergo not only C−C coupling but also C−C cleavage reactions. Thus, upon treatment of the bis(trifluoroacetates) [(η^6-mes)Os{κ^1-OC(O)CF_3}$_2$(=CR_2)] (R = C_6H_4X) with water in acetone the C−R bonds are split and the diaryl(carbonyl) complexes [(η^6-mes)OsR_2(CO)] are formed in good to excellent yields. A carbyneosmium cation is possibly involved as an intermediate, which reacts with water and/or trifluoroacetate to generate the carbonyl ligand. A labeling experiment supports this proposal. We finally note that although various osmium(0) and osmium(II) compounds with an Os=CR_2 linkage were already reported,[10−13,24,25] to the best of our knowledge the complexes **11**−**17**, **22**−**32**, and **45**, **46** are the first half-sandwich-type osmium derivatives with a non-Fischer-type carbene ligand.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by known procedures and distilled before use. The starting materials **1**,[5] **4**,[8] **8**,[26] **10**,[27] **18**,[28] and **19**[5,9] were prepared as described in the literature. NMR spectra were recorded on Bruker AC 200, Bruker DRX 300, and Bruker AMX 400 instruments. Chemical shifts are expressed in ppm downfield from TMS (^{1}H and ^{13}C{^{1}H}), 85% H_3PO_4 (^{31}P{^{1}H}), or $CFCl_3$ (^{19}F{^{1}H}). IR spectra were recorded on a Bruker IFS 25 FT-IR and mass spectra on a Finnigan MAT 90 or on a Hewlett-Packard G 1800 GCD instrument. The conductivity Λ was measured in nitromethane with a Schott Konduktometer CG 851 instrument, and melting and decomposition points were determined by DTA.

Preparation of [(η^6-mes)Os{κ^1-OC(O)CF_3}(μ-Cl)]$_2$ (2). A solution of **1** (62 mg, 0.16 mmol) in 10 mL of benzene was treated with CF_3CO_2H (18 mg, 0.16 mmol) and stirred for 1 h at room temperature. After the solvent was evaporated in vacuo, the residue was dissolved in 1 mL of CH_2Cl_2 and the solution was layered with 10 mL of hexane. Pale yellow crystals precipitated, which were separated from the mother liquor, washed twice with 5 mL portions of hexane, and dried: yield 68 mg (93%); mp 221 °C dec; Λ 63 cm^2 Ω^{-1} mol^{-1}. MS (70 eV): *m*/*z* 883 (M^+ − Cl), 805 (M^+ − CF_3CO_2), 460 (M^+/2). IR (KBr): ν(OCO) 1713, 1702, 1700, 1694 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.87, 5.76, 5.75, 5.62 (all s, CH of mes), 2.15, 2.14, 2.13, 2.08 (all s, CH_3 of mes). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 162.3 [q, J(F,C) = 33.7 Hz, CF_3CO_2], 115.4 [q, J(F,C) = 289.3 Hz, CF_3CO_2], 92.4 (s, CCH_3 of mes), 66.4 (s, CH of mes), 19.2 (s, CCH_3 of mes). ^{19}F NMR (CD_2Cl_2, 188.3 MHz): δ −78.7, −76.1, −75.8, −74.4, −74.1 (all s). Anal. Calcd for $C_{22}H_{24}Cl_2F_6O_4Os_2$ (917.7): C, 28.79; H, 2.64. Found: C, 28.70; H, 2.32.

Preparation of [(η^6-mes)Os{κ^1-OS(O)$_2CF_3$}(μ-Cl)]$_2$ (3). A solution of **1** (170 mg, 0.44 mmol) in 10 mL of THF was treated with CF_3SO_3H (66 mg, 0.44 mmol) and stirred for 2 h at room temperature. After the solvent was evaporated in vacuo, the remaining pale yellow solid was washed three times with 5 mL portions of ether and dried: yield 191 mg (88%); mp 202 °C. IR (CH_2Cl_2): ν(OSO) and ν(CF) 1382, 1160, 1156, 1032 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.04 (s, 3 H, CH of mes), 2.32 (s, 9 H, CH_3 of mes). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 118.2 [q, J(F,C) = 297.3 Hz, CF_3SO_3], 92.0 (s, CCH_3 of mes), 67.3 (s, CH of mes), 19.2 (s, CCH_3 of mes). ^{19}F NMR (CD_2Cl_2, 188.3 MHz): δ −76.4 (s). Anal. Calcd for $C_{20}H_{24}Cl_2F_6O_6Os_2S_2$ (989.8): C, 24.27; H, 2.44; S, 6.48. Found: C, 24.63; H, 2.69; S, 6.52.

Preparation of [(η^6-mes)Os{κ^1-OC(O)CF_3}$_2$(CNMe)] (5). A solution of **4** (102 mg, 0.19 mmol) in 5 mL of CH_2Cl_2 was treated with methylisocyanide (10 mg, 0.25 mmol) and stirred for 10 min at room temperature. The solvent was evaporated in vacuo, and the remaining light yellow residue was washed three times with 5 mL portions of hexane and dried: yield 97 mg (88%); mp 117 °C dec. IR (KBr): ν(CN) 2204, ν(OCO) 1697 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.47 (s, 3 H, CH of mes), 3.70 (s, 3 H, $CNCH_3$), 2.23 (s, 9 H, CH_3 of mes). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 162.8 [q, J(F,C) = 36.9 Hz, CF_3CO_2], 139.3 (s, $CNCH_3$), 113.6 [q, J(F,C) = 290.0 Hz, CF_3CO_2], 100.8 (s, CCH_3 of mes), 71.7 (s, CH of mes), 58.9 (s, $CNCH_3$), 18.5 (s, CCH_3 of mes). ^{19}F NMR (CD_2Cl_2, 188.3 MHz): δ −74.6 (s). Anal. Calcd for $C_{15}H_{15}F_6NO_4Os$ (577.5): C, 31.20; H, 2.62; N, 2.43. Found: C, 31.58; H, 2.44; N, 2.48.

Preparation of [(η^6-mes)Os{κ^1-OC(O)CF_3}$_2$(CN*t*Bu)] (6). This compound was prepared as described for **5**, from **4** (107 mg, 0.20 mmol) and CN*t*Bu (21 mg, 0.25 mmol). Pale yellow solid: yield 117 mg (95%); mp 121 °C dec. IR (KBr): ν(CN) 2187, ν(OCO) 1705, 1691 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 4.56 (s, 3 H, CH of mes), 1.67 (s, 9 H, CH_3 of mes), 1.09 [s, 9 H, $C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 162.7 [q, J(F,C) = 36.2 Hz, CF_3CO_2], 121.8 (s, $CNCCH_3$), 113.8 [q, J(F,C) = 289.7 Hz, CF_3CO_2], 100.5 (s, CCH_3 of mes), 71.5 (s, CH of mes), 58.4 (s, $CNCCH_3$), 30.2 (s, $CNCCH_3$), 18.7 (s, CCH_3 of mes). ^{19}F NMR (C_6D_6, 188.3 MHz): δ −73.9 (s). Anal. Calcd for $C_{18}H_{21}F_6NO_4Os$ (619.6): C, 34.90; H, 3.42; N, 2.26. Found: C, 34.61; H, 3.43; N, 2.18.

Preparation of [(η^6-mes)Os{κ^1-OC(O)CF_3}$_2$(PPh_3)] (7). A solution of **4** (134 mg, 0.25 mmol) in 10 mL of CH_2Cl_2 was treated with PPh_3 (79 mg, 0.30 mmol) and stirred for 15 min at room temperature. After the solution was concentrated to ca. 0.5 mL in vacuo, it was layered with 10 mL of hexane. A pale yellow solid precipitated, which was filtered, washed three times with 5 mL portions of hexane, and dried: yield 182 mg (91%); mp 138 °C dec. IR (KBr): ν(OCO) 1717, 1712 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.62, 7.57, 7.03 (all m, 15 H, C_6H_5), 5.26 (s, 3 H, CH of mes), 1.68 (s, 9 H, CH_3 of mes). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 163.2 [q, J(F,C) = 34.2 Hz, CF_3CO_2], 134.8 [d, J(P,C) = 43.3 Hz, *ipso*-C of PC_6H_5], 132.7 [d, J(P,C) = 10.1 Hz, *meta*-C of PC_6H_5], 131.0 [d, J(P,C) = 2.0 Hz, *para*-C of PC_6H_5), 128.6 [d, J(P,C) = 13.1 Hz, *ortho*-C of PC_6H_5], 114.1 [q, J(F,C) = 290.7 Hz, CF_3CO_2], 95.0 (s, CCH_3 of mes), 76.1 (s, CH of mes), 19.0 (s, CCH_3 of mes). ^{19}F NMR (CD_2Cl_2, 188.3 MHz): δ −74.3 (s). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 7.4 (s). Anal. Calcd for $C_{31}H_{27}F_6O_4OsP$: C, 46.62; H, 3.41. Found: C, 46.23; H, 3.12.

Preparation of [(η^6-tol)Os{κ^1-OC(O)CF_3}(κ^2-O_2CCF_3)] (9). A suspension of **8** (430 mg, 0.61 mmol) in 10 mL of benzene was treated with a solution of CF_3CO_2Ag (511 mg, 2.30 mmol) in 2 mL of benzene and stirred for 30 min at room temperature. The reaction mixture was filtered with Celite, and the residue was washed with 5 mL of benzene. After the filtrate was brought to dryness in vacuo, a yellow oil was obtained, which did not crystallize even after being stored for 24 h at 0 °C. The analysis of the oil revealed that the monohydrate of the product was isolated: yield 273 mg (88%). IR (CH_2Cl_2): ν(OCO) 1675, 1651, 1442, 1405 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.52 (m, 2 H, *meta*-H of $C_6H_5CH_3$), 6.24 (m, 1 H, *para*-H of $C_6H_5CH_3$), 6.12 (m, 2 H, *ortho*-H of $C_6H_5CH_3$), 2.21 (s, 3 H, $C_6H_5CH_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 165.9 [q, J(F,C)

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= 38.8 Hz, CF_3CO_2), 115.0 [q, J(F,C) = 289.9 Hz, CF_3CO_2], 89.6 (s, *ipso*-C of $C_6H_5CH_3$), 74.6 (s, *para*-C of $C_6H_5CH_3$), 67.0, 64.2 (both s, *ortho*- and *meta*-C of $C_6H_5CH_3$), 18.8 (s, $C_6H_5CH_3$). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ −75.2 (s). Anal. Calcd for $C_{11}H_{10}F_6O_5Os_2$ (526.4): C, 25.10; H, 1.91. Found: C, 24.77; H, 2.06.

Preparation of [(η^6-tol)Os{κ^1-OC(O)CF_3}$_2${=C(p-C_6H_4-Me)$_2$}] (11). A solution of **9** (107 mg, 0.21 mmol) in 2 mL of benzene was treated dropwise with a solution of (p-C_6H_4-Me)$_2CN_2$ (38 mg, 0.17 mmol) in 0.5 mL of benzene and stirred for ca. 1 min at room temperature. Both an evolution of gas (N_2) and a change of color from yellow to olive-green occurred. The solvent was evaporated in vacuo, the oily residue was dissolved in 1 mL of toluene, and the solution was layered with 10 mL of hexane. After the mixture was irradiated for ca. 3 min in an ultrasound bath, olive-green crystals precipitated, which were separated from the mother liquor, washed twice with 5 mL portions of hexane, and dried: yield 131 mg (89%); mp 123 °C dec. IR (KBr): ν(OCO) 1686, 1669, 1408 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.12, 6.88 (both m, 4 H each, C_6H_4-CH_3], 5.22 (m, 2 H, *meta*-H of $C_6H_5CH_3$), 5.10 (m, 1 H, *para*-H of $C_6H_5CH_3$), 4.70 (m, 2 H, *ortho*-H of $C_6H_5CH_3$), 2.04 (s, 6 H, $C_6H_4CH_3$), 1.70 (s, 3 H, $C_6H_5CH_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 307.0 (s, Os=C), 163.2 [q, J(F,C) = 38.1 Hz, CF_3CO_2], 156.1 (s, *ipso*-C of $C_6H_4CH_3$), 144.5 (s, *para*-C of $C_6H_4CH_3$), 131.2, 128.3 (both s, *ortho*- and *meta*-C of $C_6H_4CH_3$), 114.8 [q, J(F,C) = 290.0 Hz, CF_3CO_2], 102.3 (s, *ipso*-C of $C_6H_5CH_3$), 86.7, 82.7 (both s, *ortho*- and *meta*-C of $C_6H_5CH_3$), 74.7 (s, *para*-C of $C_6H_5CH_3$), 21.3 (s, $C_6H_4CH_3$), 17.3 (s, $C_6H_5CH_3$). ^{19}F NMR (C_6D_6, 376.5 MHz): δ −74.2 (s). Anal. Calcd for $C_{26}H_{22}F_6O_4Os$ (702.7): C, 44.44; H, 3.16. Found: C, 43.94; H, 3.66.

Preparation of [(η^6-cym)Os{κ^1-OC(O)CF_3}$_2${=C(C_6H_5)$_2$}] (12). (a) This compound was prepared as described for **11**, from **10** (66 mg, 0.12 mmol) and CPh_2N_2 (23 mg, 0.12 mmol) in 2 mL of benzene: olive-green solid; yield 92 mg (79%). (b) An alternative procedure is as follows: A solution of **18** (88 mg, 0.11 mmol) in 10 mL of benzene was treated with a solution of CF_3CO_2Ag (88 mg, 0.40 mmol) in 5 mL of benzene and stirred for 30 min at room temperature. The yellow solution was separated from the precipitate (AgCl), concentrated to ca. 1 mL in vacuo, and treated with CPh_2N_2 (78 mg, 0.40 mmol). The reaction mixture was then worked up as described for **11**: yield 122 mg (85%); mp 138 °C dec. IR (KBr): ν(OCO) 1697, 1439, 1408 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.58, 7.40, 7.20 (all m, 10 H, C_6H_5), 6.33, 5.36 [both d, J(H,H) = 6.2 Hz, 2 H each, $CH_3C_6H_4CH(CH_3)_2$], 2.83 [sept, J(H,H) = 7.0 Hz, 1 H, $CH_3C_6H_4CH(CH_3)_2$], 1.89 [s, 3 H, $CH_3C_6H_4CH(CH_3)_2$], 1.24 [d, J(H,H) = 7.0 Hz, 6 H, $CH_3C_6H_4CH(CH_3)_2$]. ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 306.1 (s, Os=C), 162.9 [q, J(F,C) = 38.1 Hz, CF_3CO_2], 159.0 (s, *ipso*-C of C_6H_5), 132.8 (s, *para*-C of C_6H_5), 131.7, 127.9 (both s, *ortho*- and *meta*-C of C_6H_5), 121.8, 99.3 (both s, *ipso*- and *para*-C of C_6H_4), 114.2 [q, J(F,C) = 291.1 Hz, CF_3CO_2], 89.0, 76.0 (both s, *ortho*- and *meta*-C of C_6H_4), 32.0 [s, $CH(CH_3)_2$], 22.0 [s, $CH(CH_3)_2$], 17.0 (s, $CH_3C_6H_4$). ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −75.3 (s). Anal. Calcd for $C_{27}H_{24}F_6O_4Os$ (716.7): C, 45.25; H, 3.38. Found: C, 45.38; H, 3.87.

Preparation of [(η^6-cym)Os{κ^1-OC(O)CF_3}$_2${=C(p-C_6H_4-Me)$_2$}] (13). This compound was prepared as described for **11**, either from **10** (66 mg, 0.12 mmol) and (p-$C_6H_4Me)_2CN_2$ (27 mg, 0.12 mmol) or from **18** (103 mg, 0.13 mmol), CF_3CO_2Ag (106 mg, 0.48 mmol), and (p-$C_6H_4Me)_2CN_2$ (107 mg, 0.48 mmol). Olive-green solid: yield 66 mg (74%) (route a) and 120 mg (67%) (route b); mp 102 °C dec. IR (KBr): ν(OCO) 1695, 1410, 1393 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.21, 7.11 [both d, J(H,H) = 8.2 Hz, 4 H each, $C_6H_4CH_3$], 6.29, 5.33 [both d, J(H,H) = 6.2 Hz, 2 H each, $CH_3C_6H_4CH(CH_3)_2$], 2.82 [sept, J(H,H) = 6.7 Hz, 1 H, $CH_3C_6H_4CH(CH_3)_2$], 2.39 (s, 6 H, $C_6H_4CH_3$), 1.87 [s, 3 H, $CH_3C_6H_4CH(CH_3)_2$], 1.23 [d, J(H,H) = 6.7 Hz, 6 H, $CH_3C_6H_4CH(CH_3)_2$]. ^{13}C NMR (CD_2Cl_2,100.6 MHz): δ 304.5 (s, Os=C), 163.3 [q, J(F,C) = 36.8 Hz, CF_3CO_2], 156.4 (s, *ipso*-C of $C_6H_4CH_3$), 144.9 (s, *para*-C of $C_6H_4CH_3$), 132.2, 128.9 (both s, *ortho*- and *meta*-C of $C_6H_4CH_3$), 120.6, 98.1 [both s, *ipso*- and *para*-C of $CH_3C_6H_4CH(CH_3)_2$], 114.5 [q, J(F,C) = 291.1 Hz, CF_3CO_2], 88.4, 75.3 [both s, *ortho*- and *meta*-C of $CH_3C_6H_4CH(CH_3)_2$], 32.2 [s, $CH_3C_6H_4CH(CH_3)_2$], 22.4, 22.1 [both s, $C_6H_4CH_3$ and $CH_3C_6H_4CH(CH_3)_2$], 17.3 [s, $CH_3C_6H_4CH(CH_3)_2$]. ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −74.5 (s). Anal. Calcd for $C_{29}H_{28}F_6O_4Os$: C, 46.77; H, 3.79. Found: C, 46.88; H, 4.26.

Preparation of [(η^6-mes)Os{κ^1-OC(O)CF_3}$_2${=C(C_6H_5)$_2$}] (14). This compound was prepared as described for **11**, from **4** (150 mg, 0.28 mmol) and (p-$C_6H_4Me)_2CN_2$ (38 mg, 0.17 mmol) in 2 mL of benzene. An olive-green solid was obtained without using the irradiation in an ultrasound bath: yield 179 mg (91%); mp 89 °C dec. IR (KBr): ν(OCO) 1709, 1674, 1664, 1439 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.60, 7.42, 7.29 (all m, 10 H, C_6H_5), 5.37 (s, 3 H, CH of mes), 2.29 [s, 9 H, CH_3 of mes). ^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ 310.3 (s, Os=C), 161.7 [q, J(F,C) = 36.9 Hz, CF_3CO_2], 158.9 (s, *ipso*-C of C_6H_5), 132.6 (s, *para*-C of C_6H_5), 130.6, 127.5 (both s, *ortho*- and *meta*-C of C_6H_5), 114.3 [q, J(F,C) = 290.7 Hz, CF_3CO_2], 106.9 (s, CCH_3 of mes), 79.8 (s, CH of mes), 18.1 (s, CCH_3 of mes). ^{19}F NMR (CD_2Cl_2, 188.3 MHz): δ −73.4 (s). Anal. Calcd for $C_{26}H_{22}F_6O_4$-Os (702.6): C, 44.44; H, 3.16. Found: C, 44.16; H, 3.29.

Preparation of [(η^6-mes)Os{κ^1-OC(O)CF_3}$_2${=C(p-C_6H_4-Me)$_2$}] (15). This compound was prepared as described for **11**, from **4** (91 mg, 0.17 mmol) and (p-$C_6H_4Me)_2CN_2$ (38 mg, 0.17 mmol) in 2 mL of benzene. Olive-green solid: yield 88 mg (71%); mp 107 °C dec. MS (70 eV): m/z (I_r) 731 (M^+), 611 (M^+ − mes). IR (CH_2Cl_2): ν(OCO) 1702, 1684, 1407 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.21, 7.16 [both d, J(H,H) = 8.2 Hz, 4 H each, $C_6H_4CH_3$], 5.33 (s, 3 H, CH of mes), 2.39 (s, 6 H, $C_6H_4CH_3$), 2.26 (s, 9 H, CH_3 of mes). ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 307.9 (s, Os=C), 161.9 [q, J(F,C) = 36.9 Hz, CF_3CO_2], 156.4 (s, *ipso*-C of $C_6H_4CH_3$), 144.6 (s, *para*-C of $C_6H_4CH_3$), 131.6, 128.4 (both s, *ortho*- and *meta*-C of $C_6H_4CH_3$), 114.6 [q, J(F,C) = 291.1 Hz, CF_3CO_2], 105.6 (s, CCH_3 of mes), 79.3 (s, CH of mes], 21.8 (s, $C_6H_4CH_3$), 18.3 (s, CCH_3 of mes). ^{19}F NMR (376.5 MHz, CD_2Cl_2): δ −75.3 (s). Anal. Calcd for $C_{28}H_{26}F_6O_4$-Os (730.7): C, 46.02; H, 3.59; Os, 26.03. Found: C, 46.21; H, 3.24; Os, 25.71.

Preparation of [(η^6-mes)Os{κ^1-OC(O)CF_3}$_2${=C(p-C_6H_4-Cl)$_2$}] (16). This compound was prepared as described for **11**, from **4** (123 mg, 0.23 mmol) and (p-$C_6H_4Cl)_2CN_2$ (61 mg, 0.23 mmol) in 2 mL of benzene. Olive-green solid: yield 103 mg (58%); mp 118 °C dec. IR (CH_2Cl_2): ν(OCO) 1665, 1662, 1434 cm^{-1}. ^{1}H NMR (CD_2Cl_2,400 MHz): δ 7.40, 7.20 [both d, J(H,H) = 8.8 Hz, 4 H each, C_6H_4Cl], 5.37 (s, 3 H, CH of mes), 2.29 (s, 9 H, CH_3 of mes). ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 305.9 (s, Os=C), 162.1 [q, J(F,C) = 37.2 Hz, CF_3CO_2], 157.4 (s, *ipso*-C of C_6H_4Cl), 139.6 (s, *para*-C of C_6H_4Cl), 131.9, 128.4 (both s, *ortho*- and *meta*-C of C_6H_4Cl), 114.5 [q, J(F,C) = 290.7 Hz, CF_3-CO_2], 108.2 (s, CCH_3 of mes), 80.2 (s, CH of mes), 18.5 (s, CCH_3 of mes). ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −75.2 (s). Anal. Calcd for $C_{26}H_{20}Cl_2F_6O_4Os$ (771.6): C, 40.47; H, 2.61. Found: C, 40.33; H, 2.63.

Preparation of [(η^6-mes)Os{κ^1-OC(O)CF_3}$_2${=C(p-C_6H_4-OMe)$_2$}] (17). A solution of **4** (86 mg, 0.16 mmol) in 2 mL of CH_2Cl_2 was treated at −78 °C with a solution of (p-C_6H_4-$OMe)_2CN_2$ (41 mg, 0.16 mmol) in 0.5 mL of CH_2Cl_2 and then slowly warmed to room temperature. Both an evolution of gas (N_2) and a change of color from yellow to brown occurred. The solvent was evaporated in vacuo and the residue worked up as described for **11**. Red-brown solid: yield 79 mg (65%); mp 120 °C dec. IR (CH_2Cl_2): ν(OCO) 1685, 1670, 1407 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.30, 6.68 [both d, J(H,H) = 8.8 Hz, 4 H each, $C_6H_4OCH_3$], 4.83 (s, 3 H, CH of mes), 3.30 (s, 6 H, OCH_3), 1.90 (s, 9 H, CH_3 of mes). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 300.1 (s, Os=C), 164.4 (s, *ipso*-C of $C_6H_4OCH_3$), 162.4 [q, J(F,C) = 36.2 Hz, CF_3CO_2], 152.0 (s, *para*-C of $C_6H_4OCH_3$), 134.8 (s, *ortho*-C of $C_6H_4OCH_3$), 115.5 [q, J(F,C) = 290.7 Hz,

CF_3CO_2], 113.3 (s, *meta*-C of $C_6H_4OCH_3$), 102.8 (s, CCH_3 of mes), 79.2 (s, CH of mes), 55.2 (s, OCH_3), 18.0 (s, CCH_3 of mes). ^{19}F NMR (C_6D_6, 376.5 MHz): δ −74.2 (s). Anal. Calcd for $C_{28}H_{26}F_6O_6Os$ (762.7): C, 44.09; H, 3.44. Found: C, 44.60; H, 3.26.

Preparation of [(η^6-cym)Os{κ^1-OS(O)$_2$C$_6$H$_4$Me-*p*}(κ^2-O$_2$S(O)C$_6$H$_4$Me-*p*)] (20). A solution of **18** (184 mg, 0.23 mmol) in 10 mL of benzene was treated with silver tosylate (246 mg, 0.88 mmol) and stirred for 24 h at room temperature. The reaction mixture was filtered with Celite, and the residue was washed with 5 mL of benzene. The filtrate was brought to dryness in vacuo, and the residue was recrystallized from benzene/hexane (1:10). A yellow hygroscopic solid was obtained, which was separated from the mother liquor, washed with small portions of hexane, and dried (the analytical data are for the trishydrate of the product): yield 197 mg (67%); mp 72 °C. IR (KBr): ν(OSO) 1209, 1204, ν(S=O) = 1127 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.61, 7.06 [both d, J(H,H) = 7.3 Hz, 4 H each, $C_6H_4CH_3$], 6.59, 6.39 [both d, J(H,H) = 4.7 Hz, 2 H each, $CH_3C_6H_4CH(CH_3)_2$], 2.71 [sept, J(H,H) = 6.7 Hz, 1 H, $CH_3C_6H_4CH(CH_3)_2$], 2.31 (s, 6 H, $C_6H_4CH_3$), 2.14 [s, 3 H, $CH_3C_6H_4CH(CH_3)_2$], 1.22 [d, J(H,H) = 6.7 Hz, 6 H, $CH_3C_6H_4CH(CH_3)_2$]. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 141.5, 139.0 (both s, *ipso*- and *para*-C of $C_6H_4CH_3$), 128.9, 126.4 (both s, *ortho*- and *meta*-C of $C_6H_4CH_3$), 90.0, 85.4 [both s, *ipso*- and *para*-C of $CH_3C_6H_4CH(CH_3)_2$], 69.8, 68.4 [both s, *ortho*- and *meta*-C of $CH_3C_6H_4CH(CH_3)_2$], 31.6 [s, $CH_3C_6H_4CH(CH_3)_2$], 22.2, 21.4 [both s, $CH_3C_6H_4CH(CH_3)_2$ and $C_6H_4CH_3$], 18.8 [s, $CH_3C_6H_4CH(CH_3)_2$]. Anal. Calcd for $C_{24}H_{28}O_6OsS_2\cdot 3H_2O$: C, 39.99; H, 4.75; S, 8.90. Found: C, 40.12; H, 4.75; S, 8.72.

Preparation of [(η^6-mes)Os{κ^1-OS(O)$_2$C$_6$H$_4$Me-*p*}(κ^2-O$_2$S(O)C$_6$H$_4$Me-*p*)] (21). This compound was prepared as described for **20**, from **19** (198 mg, 0.26 mmol) and silver tosylate (279 mg, 1.00 mmol). A pale yellow solid was isolated which proved to be the monohydrate of the product: yield 295 mg (88%); mp 152 °C. IR (C_6H_6): ν(OSO) = 1268, 1141, ν(S=O) 1102 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 8.00, 6.76 [both d, J(H,H) = 7.8 Hz, 4 H each, $C_6H_4CH_3$], 6.74 (br s, 2 H, H_2O), 4.40 (s, 3 H, CH of mes), 2.03 (s, 6 H, $C_6H_4CH_3$), 1.92 (s, 9 H, CH_3 of mes). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 140.8, 139.4 (both s, *ipso*- and *para*-C of $C_6H_4CH_3$), 128.4, 126.3 (both s, *ortho*- and *meta*-C of $C_6H_4CH_3$), 91.0 (s, CCH_3 of mes), 86.8 (s, CH of mes), 21.1 (s, $C_6H_4CH_3$), 19.3 (s, CCH_3 of mes). Anal. Calcd for $C_{23}H_{26}O_6OsS_2\cdot H_2O$ (670.8): C, 41.18; H, 4.21; S, 9.56. Found: C, 40.99; H, 4.48; S, 9.15.

Reaction of Compound 21 with PhCHN$_2$. A solution of **21** (67 mg, 0.10 mmol) in 2 mL of benzene was treated dropwise with a 1.25 M solution of $PhCHN_2$ in hexane (80 μL, 0.10 mmol) and stirred for 5 min at room temperature. An evolution of gas (N_2) occurred. The solvent was evaporated in vacuo, the oily residue was dissolved in CH_2Cl_2, and the solution was chromatographed on Al_2O_3 (basic, activity grade III). With hexane a colorless fraction was eluted, which was brought to dryness in vacuo. The white residue was identified by GC/MS and ^1H NMR data as a 1:1 mixture of *cis*- and *trans*-stilbene.[29] The same result was obtained by using **20** as the starting material.

Reaction of Compound 21 with Ph$_2$CN$_2$. A solution of **21** (67 mg, 0.10 mmol) in 3 mL of benzene was treated dropwise with a solution of Ph_2CN_2 (19 mg, 0.10 mmol) in 2 mL of benzene. While the reaction mixture was stirred for 5 min at room temperature, an evolution of gas (N_2) occurred. The solvent was evaporated in vacuo and the remaining residue identified by ^1H NMR spectroscopy and GC/MS as a mixture of **21** and $Ph_2C{=}CPh_2$.

Preparation of [(η^6-cym)OsCl$_2$(=CPh$_2$)] (22). (a) A solution of **12** (88 mg, 0.12 mmol) in 15 mL of CH_2Cl_2 was treated at −78 °C with a solution of Me_3SiCl (47 μL, 0.37 mmol) in 5 mL of CH_2Cl_2. After the reaction mixture was warmed to room temperature, it was concentrated to ca. 5 mL in vacuo and then filtered with Celite. The filtrate was brought to dryness in vacuo, and the greenish oil was dissolved in 0.5 mL of toluene. After the solution was layered with 10 mL of hexane, an olive-green solid precipitated, which was separated from the mother liquor, washed twice with 5 mL portions of hexane, and dried: yield 45 mg (67%). (b) An alternative procedure is as follows: A solution of **12** (107 mg, 0.15 mmol) in 5 mL of benzene was treated with a 1.3 M solution of HCl in benzene (0.35 mL, 0.45 mmol) and stirred for 15 min at room temperature. The solvent was evaporated in vacuo and the oily residue worked up as described for (a). Olive-green solid: yield 77 mg (92%); mp 132 °C dec. ^1H NMR (CD_2Cl_2, 400 MHz): δ 7.57, 7.39 (both m, 10 H, C_6H_5), 5.79, 5.08 [both d, J(H,H) = 6.2 Hz, 2 H each, $CH_3C_6H_4CH(CH_3)_2$], 2.89 [sept, J(H,H) = 7.0 Hz, 1 H, $CH_3C_6H_4CH(CH_3)_2$], 1.98 [s, 3 H, $CH_3C_6H_4CH(CH_3)_2$], 1.25 [d, J(H,H) = 7.0 Hz, 6 H, $CH_3C_6H_4CH(CH_3)_2$]. ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 300.7 (s, Os=C), 163.0 (s, *ipso*-C of C_6H_5), 132.0 (s, *para*-C of C_6H_5), 130.0, 127.3 (both s, *ortho*- and *meta*-C of C_6H_5), 119.9, 102.8 [both s, *ipso*- and *para*-C of $CH_3C_6H_4CH(CH_3)_2$], 90.9, 80.7 [both s, *ortho*- and *meta*-C of $CH_3C_6H_4CH(CH_3)_2$], 31.1 [s, $CH_3C_6H_4CH(CH_3)_2$], 22.2 [s, $CH_3C_6H_4CH(CH_3)_2$], 17.3 [s, $CH_3C_6H_4CH(CH_3)_2$]. Anal. Calcd for $C_{23}H_{24}Cl_2Os$ (561.6): C, 49.19; H, 4.31. Found: C, 48.87; H, 4.28.

Preparation of [(η^6-cym)OsCl$_2${=C(*p*-C$_6$H$_4$Me)$_2$}] (23). This compound was prepared as described for **22**, from **13** (93 mg, 0.12 mmol) and Me_3SiCl (51 μL, 0.40 mmol). Olive-green solid: yield 54 mg (76%); mp 144 °C dec. ^1H NMR (CD_2Cl_2, 400 MHz): δ 7.32, 7.18 [both d, J(H,H) = 8.2 Hz, 4 H each, $C_6H_4CH_3$], 5.77, 5.03 [both d, J(H,H) = 6.2 Hz, 2 H each, $CH_3C_6H_4CH(CH_3)_2$], 2.90 [sept, J(H,H) = 7.0 Hz, 1 H, $CH_3C_6H_4CH(CH_3)_2$], 2.37 [s, 3 H, $CH_3C_6H_4CH(CH_3)_2$], 1.93 (s, 6 H, $C_6H_4CH_3$), 1.25 [d, J(H,H) = 7.0 Hz, 6 H, $CH_3C_6H_4CH(CH_3)_2$]. ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 299.3 (s, Os=C), 159.9 (s, *ipso*-C of $C_6H_4CH_3$), 143.4 (s, *para*-C of $C_6H_4CH_3$), 131.0, 127.9 (both s, *ortho*- and *meta*-C of $C_6H_4CH_3$), 118.7, 101.2 [both s, *ipso*- and *para*-C of $CH_3C_6H_4CH(CH_3)_2$], 90.0, 79.0 [both s, *ortho*- and *meta*-C of $CH_3C_6H_4CH(CH_3)_2$], 30.9 [s, $CH_3C_6H_4CH(CH_3)_2$], 22.1, 21.6 [boths s, $C_6H_4CH_3$ and $CH_3C_6H_4CH(CH_3)_2$], 17.0 [s, $CH_3C_6H_4CH(CH_3)_2$]. Anal. Calcd for $C_{25}H_{28}Cl_2Os$ (589.6): C, 50.93; H, 4.77. Found: C, 50.91; H, 4.45.

Preparation of [(η^6-cym)OsBr$_2$(=CPh$_2$)] (24). This compound was prepared as described for **22**, either from **12** (72 mg, 0.10 mmol) and Me_3SiBr (53 μL, 0.40 mmol) or from **12** (72 mg, 0.10 mmol) and a 0.7 M solution of HBr in benzene (0.36 mL, 0.25 mmol). Brown solid: yield 56 mg (86%) (route a) and 48 mg (74%) (route b); mp 132 °C dec. ^1H NMR (C_6D_6, 400 MHz): δ 7.46, 7.05 (both m, 10 H, C_6H_5), 5.44, 4.45 [both d, J(H,H) = 5.6 Hz, 2 H each, $CH_3C_6H_4CH(CH_3)_2$], 2.98 [sept, J(H,H) = 6.8 Hz, 1 H, $CH_3C_6H_4CH(CH_3)_2$], 1.36 [s, 3 H, $CH_3C_6H_4CH(CH_3)_2$], 1.02 [d, J(H,H) = 6.8 Hz, 6 H, $CH_3C_6H_4CH(CH_3)_2$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 299.9 (s, Os=C), 165.4 (s, *ipso*-C of C_6H_5), 131.3 (s, *para*-C of C_6H_5), 129.4, 126.7 (both s, *ortho*- and *meta*-C of C_6H_5), 120.2, 102.1 (both s, *ipso*- and *para*-C of C_6H_4), 91.4, 79.7 (both s, *ortho*- and *meta*-C of C_6H_4), 30.1 [s, $CH(CH_3)_2$], 22.4 [s, $CH(CH_3)_2$], 17.0 (s, $CH_3C_6H_4$). Anal. Calcd for $C_{23}H_{24}Br_2Os$ (650.5): C, 42.47; H, 3.72. Found: C, 42.15; H, 3.35.

Preparation of [(η^6-cym)OsBr$_2${=C(*p*-C$_6$H$_4$Me)$_2$}] (25). This compound was prepared as described for **22**, from **13** (62 mg, 0.08 mmol) and Me_3SiBr (53 μL, 0.40 mmol). Brown solid: yield 39 mg (72%), mp 147 °C dec. ^1H NMR (CD_2Cl_2, 400 MHz): δ 7.35, 7.20 [both d, J(H,H) = 8.2 Hz, 4 H each, $C_6H_4CH_3$], 5.95, 5.17 [both d, J(H,H) = 6.2 Hz, 2 H each, $CH_3C_6H_4CH(CH_3)_2$], 3.05 [sept, J(H,H) = 7.0 Hz, 1 H, $CH_3C_6H_4CH(CH_3)_2$], 2.39 (s, 6 H, $C_6H_4CH_3$), 1.95 [s, 3 H, $CH_3C_6H_4CH(CH_3)_2$], 1.29 [d, J(H,H) = 7.0 Hz, 6 H, $CH_3C_6H_4CH(CH_3)_2$]. ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 299.4 (s, Os=

(29) Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der Organischen Chemie*, 4th ed.; Thieme: Stuttgart, 1991.

C), 161.9 (s, *ipso*-C of $C_6H_4CH_3$), 143.5 (s, *para*-C of $C_6H_4CH_3$), 130.9, 128.0 (both s, *ortho*- and *meta*-C of $C_6H_4CH_3$), 119.5, 102.4 [both s, *ipso*- and *para*-C of $CH_3C_6H_4CH(CH_3)_2$], 90.5, 78.8 [both s, *ortho*- and *meta*-C of $CH_3C_6H_4CH(CH_3)_2$], 31.3 [s, $CH_3C_6H_4CH(CH_3)_2$], 22.5, 21.8 [both s, $C_6H_4CH_3$ and $CH_3C_6H_4CH(CH_3)_2$], 17.4 [s, $CH_3C_6H_4CH(CH_3)_2$]. Anal. Calcd for $C_{25}H_{28}Br_2Os$ (678.5): C, 44.25; H, 4.16. Found: C, 44.33; H, 4.00.

Preparation of [(η^6-cym)OsI_2(=CPh_2)] (26). A solution of **10** (95 mg, 0.13 mmol) in 40 mL of CH_2Cl_2 was treated with NH_4I (188 mg, 1.30 mmol) and stirred for 8 h at room temperature. The reaction mixture was filtered with Celite, and the filtrate was concentrated to ca. 1 mL in vacuo. After the solution was layered with 10 mL of hexane, a red-brown solid precipitated, which was separated from the mother liquor, washed twice with 5 mL portions of hexane, and dried: yield 66 mg (68%); mp 132 °C dec. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.55, 7.31 (both m, 10 H, C_6H_5), 6.11, 5.41 [both d, J(H,H) = 5.8 Hz, 2 H each, $CH_3C_6H_4CH(CH_3)_2$], 3.12 [sept, J(H,H) = 6.9 Hz, 1 H, $CH_3C_6H_4CH(CH_3)_2$], 2.00 [s, 3 H, $CH_3C_6H_4CH(CH_3)_2$], 1.24 [d, J(H,H) = 6.9 Hz, 6 H, $CH_3C_6H_4CH(CH_3)_2$]. ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 297.3 (s, Os=C), 168.5 (s, *ipso*-C of C_6H_5), 131.2 (s, *para*-C of C_6H_5), 128.4, 127.2 (both s, *ortho*- and *meta*-C of C_6H_5), 121.5, 106.5 (both s, *ipso*- and *para*-C of C_6H_4), 90.9, 82.0 [both s, *ortho*- and *meta*-C of C_6H_4), 31.9 [s, $CH(CH_3)_2$], 22.7 [s, $CH(CH_3)_2$], 18.0 (s, $CH_3C_6H_4$). Anal. Calcd for $C_{23}H_{24}I_2Os$ (744.5): C, 37.11; H, 3.25. Found: C, 36.76; H, 3.10.

Preparation of [(η^6-cym)OsI_2{=C(p-$C_6H_4Me)_2$}] (27). This compound was prepared as described for **26**, from **13** (60 mg, 0.08 mmol) and NH_4I (116 mg, 0.80 mmol). Red-brown solid: yield 56 mg (91%), mp 134 °C dec. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.23, 7.10 [both d, J(H,H) = 7.9 Hz, 4 H each, $C_6H_4CH_3$], 6.09, 5.34 [both d, J(H,H) = 6.2 Hz, 2 H each, $CH_3C_6H_4CH(CH_3)_2$], 3.14 [sept, J(H,H) = 7.0 Hz, 1 H, $CH_3C_6H_4CH(CH_3)_2$], 2.32 (s, 6 H, $C_6H_4CH_3$), 1.94 [s, 3 H, $CH_3C_6H_4CH(CH_3)_2$], 1.24 [d, J(H,H) = 7.0 Hz, 6 H, $CH_3C_6H_4CH(CH_3)_2$]. ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 297.3 (s, Os=C), 165.4 (s, *ipso*-C of $C_6H_4CH_3$), 142.8 (s, *para*-C of $C_6H_4CH_3$), 130.0, 127.8 (both s, *ortho*- and *meta*-C of $C_6H_4CH_3$), 120.2, 104.8 [both s, *ipso*- and *para*-C of $CH_3C_6H_4CH(CH_3)_2$], 90.2, 80.4 [both s, *ortho*- and *meta*-C of $CH_3C_6H_4CH(CH_3)_2$], 31.9 [s, $CH_3C_6H_4CH(CH_3)_2$], 22.8, 21.8 [both s, $C_6H_4CH_3$ and $CH_3C_6H_4CH(CH_3)_2$], 17.8 [s, $CH_3C_6H_4CH(CH_3)_2$]. Anal. Calcd for $C_{25}H_{28}I_2Os$ (772.5): C, 38.87; H, 3.65. Found: C, 38.51; H, 3.17.

Preparation of [(η^6-mes)$OsCl_2$(=CPh_2)] (28). This compound was prepared as described for **22**, either from **14** (136 mg, 0.19 mmol) and Me_3SiCl (72 μL, 0.57 mmol) or from **14** (136 mg, 0.19 mmol) and a 1.3 M solution of HCl in benzene (0.38 mL, 0.50 mmol). Olive-green solid: yield 82 mg (79%) (route a) and 90 mg (87%) (route b); mp 126 °C dec. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.58, 7.38, 7.37 (all m, 10 H, C_6H_5), 4.97 (s, 3 H, CH of mes), 2.27 (s, 9 H, CH_3 of mes). ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 299.2 (s, Os=C), 163.8 (s, *ipso*-C of C_6H_5), 131.9 (s, *para*-C of C_6H_5), 130.1, 127.6 (both s, *ortho*- and *meta*-C of C_6H_5), 108.7 (s, CCH_3 of mes), 82.6 (s, CH of mes), 18.2 (s, CCH_3 of mes). Anal. Calcd for $C_{22}H_{22}Cl_2Os$ (547.5): C, 48.26; H, 4.05. Found: C, 48.66; H, 4.17.

Preparation of [(η^6-mes)$OsCl_2${=C(p-$C_6H_4Me)_2$}] (29). This compound was prepared as described for **22**, from **15** (88 mg, 0.12 mmol) and Me_3SiCl (70 μL, 0.55 mmol). Olive-green solid: yield 60 mg (87%); mp 153 °C dec. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.38, 6.98 [both d, J(H,H) = 8.0 Hz, 4 H each, $C_6H_4CH_3$], 4.78 (s, 3 H, CH of mes), 2.09 (s, 6 H, $C_6H_4CH_3$), 2.00 (s, 9 H, CH_3 of mes). ^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ 302.8 (s, Os=C), 158.1 (s, *ipso*-C of $C_6H_4CH_3$), 143.9 (s, *para*-C of $C_6H_4CH_3$), 131.0, 128.3 (both s, *ortho*- and *meta*-C of $C_6H_4CH_3$), 106.6 (s, CCH_3 of mes), 80.3 (s, CH of mes), 21.7 (s, $C_6H_4CH_3$), 18.3 (s, $CCH_3$of mes). Anal. Calcd for $C_{24}H_{26}Cl_2Os$ (575.6): C, 50.08; H, 4.55. Found: C, 50.37; H, 4.25.

Preparation of [(η^6-mes)$OsCl_2${=C(p-$C_6H_4OMe)_2$}] (30). This compound was prepared as described for **22**, from **17** (92 mg, 0.12 mmol) and Me_3SiCl (48 μL, 0.36 mmol). Red-brown solid: yield 60 mg (82%); mp 137 °C dec. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.59, 6.66 [both d, J(H,H) = 8.8 Hz, 4 H each, $C_6H_4OCH_3$], 4.37 (s, 3 H, CH of mes), 3.27 (s, 6 H, OCH_3), 1.94 (s, 9 H, CH_3 of mes). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 163.5 (s, *ipso*-C of $C_6H_4OCH_3$), 156.4 (s, *para*-C of $C_6H_4OCH_3$), 132.4 (s, *ortho*-C of $C_6H_4OCH_3$), 112.6 (s, *meta*-C of $C_6H_4OCH_3$), 105.2 (s, CCH_3 of mes), 80.2 (s, CH of mes), 54.8 (s, OCH_3), 18.9 (s, CCH_3 of mes), signal for Os=C carbon atom not exactly located. Anal. Calcd for $C_{24}H_{26}Cl_2O_2Os$ (607.6): C, 47.44; H, 4.31. Found: C, 47.77; H, 4.04.

Preparation of [(η^6-mes)OsI_2(=CPh_2)] (31). A solution of **14** (105 mg, 0.15 mmol) in 5 mL of benzene was treated with Me_3SiI (60 mg, 0.30 mmol) and stirred for 5 min at room temperature. A change of color from dark green to red occurred. The reaction mixture was filtered with Celite, and the filtrate was brought to dryness in vacuo. The residue was dissolved in 1 mL of CH_2Cl_2, and the solution was layered with 10 mL of hexane. Red crystals precipitated, which were separated from the mother liquor, washed twice with 5 mL portions of ether, and dried: yield 79 mg (72%); mp 98 °C dec. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.38, 7.34, 6.97 (all m, 10 H, C_6H_5), 4.48 (s, 3 H, CH of mes), 2.03 (s, 9 H, CH_3 of mes). ^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ 296.8 (s, Os=C), 169.6 (s, *ipso*-C of C_6H_5), 131.0 (s, *para*-C of C_6H_5), 127.9, 127.1 (both s, *ortho*- and *meta*-C of C_6H_5), 106.4 (s, CCH_3 of mes), 85.9 (s, CH of mes), 20.3 (s, CCH_3 of mes). Anal. Calcd for $C_{22}H_{22}I_2Os$ (730.4): C, 36.18; H, 3.04. Found: C, 35.83; H, 2.94.

Preparation of [(η^6-mes)$OsBr_2$(=CPh_2)] (32). A solution of **14** (100 mg, 0.14 mmol) in 5 mL of benzene was treated with a 0.7 M solution of HBr in benzene (0.31 mL, 0.40 mmol) and stirred for 15 min at room temperature. The solvent was evaporated in vacuo, and the oily residue was dissolved in 0.5 mL of CH_2Cl_2. Addition of 10 mL of hexane led to the precipitation of a brown solid, which was separated from the mother liquor, washed twice with 3 mL portions of hexane, and dried: yield 62 mg (70%); mp 138 °C dec. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.56, 7.39, 7.04 (all m, 10 H, C_6H_5), 4.31 (s, 3 H, CH of mes), 1.92 (s, 9 H, CH_3 of mes). Anal. Calcd for $C_{22}H_{22}Br_2Os$ (636.4): C, 41.52; H, 3.48. Found: C, 41.96; H, 3.35.

Preparation of [(η^6-mes)OsCl(κ^2-acac)] (33). (a) A solution of **28** (55 mg, 0.10 mmol) in 10 mL of benzene was treated with Tl(acac) (30 mg, 0.10 mmol) and stirred for 2 h at room temperature. After the reaction mixture was concentrated in vacuo to ca. 0.5 mL, it was chromatographed on Al_2O_3 (basic, activity grade III). With benzene a yellow fraction was eluted, which was concentrated in vacuo to ca. 0.5 mL. Addition of hexane (20 mL) led to the precipitation of yellow crystals, which were separated from the mother liquor, washed twice with 5 mL portions of hexane, and dried: yield 28 mg (64%). (b) A suspension of **19** (53 mg, 0.07 mmol) in 20 mL of benzene was treated with both acetylacetone (72 μL, 0.70 mmol) and NEt_3 (50 μL, 0.36 mmol) and stirred for 30 min at 80 °C. The reaction mixture was filtered with Celite and the residue washed twice with 5 mL portions of benzene. The combined filtrates were brought to dryness in vacuo, the remaining yellow solid was washed twice with 5 mL portions of hexane and dried: yield 58 mg (93%); mp 156 °C. The product was identified by comparison of the IR and ^{1}H NMR data with those reported in the literature.[16] ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 186.3 (s, CCH_3 of acac), 100.9 (s, CH of acac), 93.7 (s, CCH_3 of mes), 65.4 (s, CH of mes), 27.8 (s, CH_3 of acac), 18.5 (s, CCH_3 of mes).

Preparation of [(η^6-mes)OsCl(κ^2-acac-[F_3])] (34). This compound was prepared as described for **33**, either from **28** (82 mg, 0.15 mmol) and Na(acac-[F_3]) (26 mg, 0.15 mmol) in 10 mL of benzene or from **19** (76 mg, 0.10 mmol) and Na(acac-[F_3]) (53 mg, 0.30 mmol) in 10 mL of MeOH. Red-brown solid: yield 28 mg (38%) (route a) and 93 mg (93%) (route b); mp

218 °C dec. IR (KBr): ν(CO) 1616 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.67 (s, 3 H, CH of mes), 5.51 (s, 1 H, CH of acac-[F_3]), 2.14 (s, 9 H, CH_3 of mes), 2.06 (s, 3 H, CH_3 of acac-[F_3]). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 192.9 (s, *C*CH_3 of acac-[F_3]), 166.2 (q, J(F,C) = 34.2 Hz, *C*CF_3 of acac-[F_3]), 117.6 [q, J(F,C) = 282.9 Hz, CF_3], 96.3 (br s, CH of acac-[F_3]), 93.8 (s, *C*CH_3 of mes), 65.1 (s, CH of mes), 28.6 (s, C*C*H_3 of acac-[F_3]), 17.9 (s, CH_3 of mes). ^{19}F NMR ($CDCl_3$, 188.3 MHz): δ −74.9 (s). Anal. Calcd for $C_{14}H_{16}ClF_3O_2Os$ (499.0): C, 33.70; H, 3.23. Found: C, 33.44; H, 2.98.

Preparation of [(η^6-mes)OsCl(κ^2-acac-[F_6])] (35). This compound was prepared as described for **33**, either from **28** (93 mg, 0.17 mmol) and Na(acac-[F_6]) (39 mg, 0.17 mmol) in 10 mL of benzene or from **19** (61 mg, 0.08 mmol) and Na(acac-[F_6]) (55 mg, 0.24 mmol) in 10 mL of MeOH. Red solid: yield 40 mg (43%) (route a) and 80 mg (90%) (route b); mp 229 °C dec. IR (KBr): ν(CO) 1623 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.02 (s, 1 H, CH of acac-[F_6]), 5.63 (s, 3 H, CH of mes), 2.19 (s, 9 H, CH_3 of mes). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 172.7 [q, J(F,C) = 36.0 Hz, *C*CF_3], 116.9 [q, J(F,C) = 283.8 Hz, CF_3], 95.0 (s, *C*CH_3 of mes), 92.4 (br s, CH of acac-[F_6]), 65.9 (s, CH of mes), 18.0 (s, C*C*H_3 of mes). ^{19}F NMR ($CDCl_3$, 188.3 MHz): δ −75.6 (s). Anal. Calcd for $C_{14}H_{13}ClF_6O_2Os$ (552.9): C, 30.41; H, 2.37. Found: C, 30.25; H, 2.25.

Reaction of Compound 28 with C_6H_5MgBr. A solution of **28** (71 mg, 0.13 mmol) in 5 mL of THF was treated at −78 °C with a 1.62 M solution of C_6H_5MgBr in THF (0.34 mL, 0.54 mmol). After the reaction mixture was stirred for 15 min, it was slowly warmed to room temperature, and then the solvent was evaporated in vacuo. The residue was recrystallized from CH_2Cl_2/hexane to give **32** as the sole product: yield 49 mg (59%). A similar result was obtained by using compound **14** as the starting material; yield 64%.

Reaction of Compound 28 with CH_3MgI. A solution of **28** (66 mg, 0.12 mmol) in 5 mL of THF was treated at −78 °C with a 1.88 M solution of CH_3MgI in THF (0.26 mL, 0.50 mmol). After the reaction mixture was stirred for 15 min, it was slowly warmed to room temperature. The solvent was evaporated in vacuo, and the residue was extracted with 5 mL of toluene. The extract was concentrated to ca. 0.5 mL in vacuo, and the solution was layered with 10 mL of pentane. A red solid precipitated, which was shown by ^{1}H NMR spectroscopy to be **32**: yield 45 mg (51%). A similar result was obtained by using compound **14** as the starting material; yield 66%.

Preparation of [(η^6-mes)OsBr(η^3-CH_2CHCPh_2)] (36). A solution of **11** (84 mg, 0.12 mmol) in 5 mL of THF was treated at −78 °C with a 1.88 M solution of CH_3MgI in THF (0.50 mL, 0.25 mmol). While the reaction mixture was stirred for 30 min, it was slowly warmed to room temperature and then filtered with Celite. The filtrate was brought to dryness in vacuo, and the residue was dissolved in 2 mL of benzene. The solution was chromatographed on Al_2O_3 (basic, activity grade III). With benzene/hexane (1:1) a yellow fraction was eluted, from which the solvent was evaporated in vacuo. The oily residue was dissolved in 1 mL of hexane and the solution stored at −78 °C. A pale yellow solid precipitated, which was separated from the mother liquor, washed with small quantities of pentane (−20 °C), and dried: yield 43 mg (61%); mp 94 °C dec. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.69, 7.34, 7.11, 7.01 (all m, 10 H, C_6H_5), 5.00 [dd, J(H^1,H^3) = 8.8, J(H^1,H^2) = 6.7 Hz, 1 H, $CH_2CH^1CPh_2$], 4.51 (s, 3 H, CH of mes), 2.75 [dd, J(H^1,H^2) = 6.7, J(H^2,H^3) = 1.5 Hz, 1 H, H^2 of CH_2 *cis* to H^1], 2.42 [dd, J(H^1,H^3) = 8.8, J(H^2,H^3) = 1.5 Hz, 1 H, H^3 of CH_2 *trans* to H^1], 1.59 (s, 9 H, CH_3 of mes). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 160.1 (s, *ipso*-C of C_6H_5), 138.8, 136.4, 129.8, 129.7, 129.1, 128.7, 128.3 (all s, C_6H_5), 93.2 (s, *C*CH_3 of mes), 76.7 (s, CH of mes), 74.5(s, CH_2CHCPh_2), 66.1 (s, *C*C_6H_5), 33.8 (s, *C*H_2CHCPh_2), 18.4 (s, C*C*H_3 of mes). Anal. Calcd for $C_{24}H_{25}BrOs$ (583.6): C, 49.40; H, 4.32. Found: C, 49.82; H, 4.58.

Reaction of Compound 36 with CF_3CO_2H. A solution of **36** (76 mg, 0.13 mmol) in 5 mL of benzene was treated with CF_3CO_2H (15 mg, 0.13 mmol) and stirred for 30 min at room temperature. After the solvent was evaporated in vacuo, the residue was extracted with 10 mL of hexane. The extract was concentrated to ca. 1 mL, and the solution was chromatographed on Al_2O_3 (basic, activity grade III). With benzene a colorless fraction was eluted, which after removal of the solvent gave a white solid, identified by comparison of the NMR spectroscopic data with those of an authentic sample[30] as Ph_2C=CHMe: yield 21 mg (84%). The ^{1}H and ^{19}F NMR spectroscopic data of the solid residue (from which the olefin was extracted) indicate the presence of a mixture of products containing [(η^6-mes)OsBr(κ^2-O_2CCF_3)] (**37**) as the major component. Data for **37**: ^{1}H NMR (C_6D_6, 200 MHz): δ 4.70 (s, 3 H, CH of mes), 1.30 (s, 9 H, CH_3 of mes). ^{19}F NMR (C_6D_6, 188.3 MHz): δ −74.9 (s).

Preparation of [(η^6-mes)Os{κ^2(*C*,*O*)-Ph_2*C*CH=CH*O*Et}-{κ^1-OC(O)CF_3}] (38). A solution of **14** (115 mg, 0.16 mmol) in 5 mL of ethyl(vinyl)ether was treated with Na_2CO_3 (200 mg, 1.89 mmol) and stirred for 3.5 h at room temperature. A slow change of color from dark green to brown occurred. After the solvent was evaporated in vacuo, the residue was extracted with 20 mL of benzene/hexane (1:1), and then the extract was brought to dryness in vacuo. A pale brown solid was obtained, which was washed twice with 5 mL portions of hexane (0 °C) and dried: yield 84 mg (78%); mp 104 °C dec. IR (KBr): ν(OCO) 1691, ν(C=C) 1596 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.39, 7.13, 7.00, 6.88 (all m, 10 H, C_6H_5), 5.88 [d, J(H,H) = 7.4 Hz, 1 H, OC*H*=CHR], 5.28 [d, J(H,H) = 7.4 Hz, 1 H, OCH=C*H*R], 4.84 (s, 3 H, CH of mes), 3.86, 3.47 [both dq, ^2J(H,H) = 10.0, ^3J(H,H) = 7.2 Hz, 1 H each, OCH_2CH_3], 1.51 (s, 9 H, CH_3 of mes), 1.12 [t, J(H,H) = 7.2 Hz, 3 H, OCH_2CH_3]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 163.0 [q, J(C,F) = 36.0 Hz, CF_3CO_2], 148.1 (s, O*C*H=CHR), 142.8 (s, OCH=*C*HR), 132.6, 128.3, 128.2, 127.4, 126.1, 125.0, 108.3 (all s, C_6H_5), 114.6 [q, J(C,F) = 290.9 Hz, *C*F_3CO_2], 93.1 (s, *C*CH_3 of mes), 81.6 (s, CH of mes), 68.2 (s, O*C*H_2CH_3), 61.7 (s, Os*C*Ph_2), 17.2 (s, C*C*H_3 of mes), 15.1 (s, OCH_2*C*H_3). ^{19}F NMR (CD_2Cl_2, 188.3 MHz): δ −74.7 (s). Anal. Calcd for $C_{28}H_{29}F_3O_3Os$ (660.7): C, 50.90; H, 4.42. Found: C, 50.62; H, 4.08.

Reaction of Compound 38 with CF_3CO_2H. A solution of **38** (92 mg, 0.14 mmol) in 5 mL of benzene was treated with CF_3CO_2H (16 mg, 0.14 mmol) and stirred for 30 min at room temperature. After the solvent was evaporated in vacuo, the residue was extracted with 10 mL of hexane. The extract was concentrated to ca. 1 mL, and the solution was chromatographed on Al_2O_3 (basic, activity grade III). With benzene a colorless fraction was eluted, which after removal of the solvent gave a white solid, identified by comparison of the NMR spectroscopic data with those of an authentic sample[31] as Ph_2C=CHCH_2OEt: yield 24 mg (72%). The ^{1}H and ^{19}F NMR spectroscopic data of the solid residue (from which the olefin was extracted) indicate the presence of a mixture of products containing **4** as the major component.

Preparation of [(η^6-mes)Os(C_6H_5)$_2$(CO)] (39). A solution of **14** (142 mg, 0.20 mmol) in 3 mL of acetone was treated with water (100 μL, 5.45 mmol) and stirred for 5 h at room temperature. A slow change of color from green to yellow occurred. After the solvent was evaporated in vacuo, the residue was dissolved in 2 mL of hexane/CH_2Cl_2 (1:1) and the solution chromatographed on Al_2O_3 (basic, activity grade III). With hexane/CH_2Cl_2 (1:1) a yellow fraction was eluted, which was brought to dryness in vacuo. The remaining yellow solid was washed twice with 5 mL portions of hexane and dried: yield 89 mg (89%). It was identified by comparison of the IR and ^{1}H NMR spectroscopic data with those of an authentic sample as **39**.[19] Formerly unpublished data for **39**: ^{13}C NMR

(30) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *J. Am. Chem. Soc.* **1986**, *108*, 2641−2645.
(31) Eisch, J. J.; Merkley, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 1148−1155.

Table 1. Crystallographic Data for 2, 28, and 35

	2	28	35
formula	$C_{22}H_{24}Cl_2F_6O_4Os_2$	$C_{22}H_{22}Cl_2Os + 1/2CH_2Cl_2$	$C_{14}H_{13}ClF_6O_2Os$
fw	917.73	589.96	552.89
cryst size,mm	0.24 × 0.18 × 0.16	0.3 × 0.2 × 0.2	0.22 × 0.20 × 0.18
cryst syst	monoclinic	monoclinic	triclinic
space group	*C*2/*c* (No. 15)	*C*2 (No. 5)	$P\bar{1}$ (No. 2)
cell dimens determn	25 rflns, 49.5° < θ < 50.0°	25 rflns, 10° < θ < 15°	5000 rflns, 2.57° < θ < 25.03°
a, Å	10.066(2)	18.282(1)	8.719(8)
b, Å	12.935(2)	7.710(1)	8.774(5)
c, Å	20.197(2)	15.709(1)	12.132(8)
α, deg	90	90	89.12(8)
β, deg	94.54(1)	105.05(2)	76.50(9)
γ, deg	90	90	65.23(9)
V, Å^3	2621.5(5)	2138.3(3)	816(1)
Z	4	4	2
d_{calcd}, g cm^{-1}	2.325	1.833	2.251
temp, K	296(2)	273(2)	173(2)
μ, mm^{-1}	20.585	6.343	8.046
scan method	$\omega-2/\theta$	ω/θ	ϕ
2θ(max), deg	59.94	52.02	50.06
total no. of rflns	2186	7562	6253
no. of unique rflns	1951 (*R*(int) = 0.08528)	3808 (*R*(int) = 0.0311)	2716 (*R*(int) = 0.0256)
no. of obsd rflns	1860 ($I > 2\sigma(I)$)	3479 ($I > 2\sigma(I)$)	2444 ($I > 2\sigma(I)$)
no. of rflns used for refinement	1951	3808	2716
no. of params refined	165	243	224
final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0369$, $wR_2 = 0.0567$[a]	$R_1 = 0.0206$, $wR_2 = 0.0443$[a]	$R_1 = 0.0186$, $wR_2 = 0.0418$[a]
R indices (all data)	$R_1 = 0.0381$, $wR_2 = 0.0569$[a]	$R_1 = 0.0263$, $wR_2 = 0.0481$[a]	$R_1 = 0.0225$, $wR_2 = 0.0427$[a]
resid electron density, e Å^{-3}	1.41/−1.30	0.696/−0.947	0.860/−0.948

[a] $w^{-1} = [\sigma^2F_o^2 + (0.00022P)^2 + 0.0000P]$ (**2**), $w^{-1} = [\sigma^2F_o^2 + (0.0321P)^2 + 0.0321P]$ (**28**), $w^{-1} = [\sigma^2F_o^2 + (0.0256P)^2 + 0.0000P]$ (**35**), where $P = (F_o^2 + 2F_c^2)/3$.

(C_6D_6, 100.6 MHz): δ 185.1 (s, CO), 142.9 (s, *ipso*-C of C_6H_5), 128.3, 127.7, 122.7 (all s, C_6H_5), 112.4 (s, *C*CH_3 of mes), 86.9 (s, CH of mes), 18.7 (s, C*C*H_3 of mes).

Preparation of [(η^6-mes)Os(C_6H_5)$_2$($C^{18}O$)] (39a). This compound was prepared as described for **39**, from **14** (171 mg, 0.24 mmol) and $H_2{}^{18}O$ (100 μL, 4.75 mmol) in 5 mL of acetone. After the solvent was removed, the residue was characterized spectroscopically. The IR spectrum (in CH_2Cl_2) displayed two strong absorptions at 1946 and 1904 cm^{-1} in the approximate ratio of 2:1 assigned to **39** and **39a**, respectively.

Preparation of [(η^6-mes)Os(*p*-C_6H_4Me)$_2$(CO)] (40). This compound was prepared as described for **39**, from **15** (63 mg, 0.09 mmol) and water (50 μL, 2.77 mmol). Yellow solid: yield 29 mg (61%); mp 116 °C dec. IR (KBr): ν(CO) 1924 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.40, 6.71 [both d, *J*(H,H) = 8.0 Hz, 4 H each, C_6H_4], 5.22 (s, 3 H, CH of mes), 2.19 (s, 6 H, $C_6H_4CH_3$), 2.04 (s, 9 H, CH_3 of mes). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 184.8 (s, CO), 142.0 (s, *ipso*-C of C_6H_4), 134.3 (s, *para*-C of C_6H_4), 130.8, 128.3 (both s, *ortho*- and *meta*-C of C_6H_4), 112.7 (s, *C*CH_3 of mes), 86.9 (s, CH of mes), 20.7 (s, $C_6H_4CH_3$), 19.1 (s, C*C*H_3 of mes). Anal. Calcd for $C_{24}H_{26}OOs$ (520.7): C, 55.36; H, 5.03. Found: C, 55.21; H, 4.92.

Preparation of [(η^6-mes)Os(*p*-C_6H_4OMe)$_2$(CO)] (41). This compound was prepared as described for **39**, from **17** (84 mg, 0.11 mmol) and water (50 μL, 2.77 mmol). Yellow solid: yield 44 mg (72%); mp 121 °C dec. IR (KBr): ν(CO) 1942 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.33, 6.88 [both d, *J*(H,H) = 8.0 Hz, 4 H each, C_6H_4], 4.64 (s, 3 H, CH of mes), 3.83 (s, 6 H, OCH_3), 2.13 (s, 9 H, CH_3 of mes). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 179.1 (s, CO), 157.7 (s, *para*-C of C_6H_4), 139.8 (s, *ipso*-C of C_6H_4), 131.1 (s, *ortho*-C of C_6H_4), 113.1 (s, *meta*-C of C_6H_4), 97.4 (s, *C*CH_3 of mes), 74.8 (s, CH of mes), 55.3 (s, OCH_3), 19.8 (s, C*C*H_3 of mes). Anal. Calcd for $C_{24}H_{26}O_3Os$ (552.7): C, 52.16; H, 4.74. Found: C, 52.07; H, 4.58.

Reactions of Compound 28 with P*i*Pr$_3$, As*i*Pr$_3$, and Sb*i*Pr$_3$. A solution of 28 (49 mg, 0.09 mmol) in 10 mL of benzene was treated with a 2-fold excess of P*i*Pr$_3$, As*i*Pr$_3$, or Sb*i*Pr$_3$ and stirred for 3 h at 80 °C. The solvent was evaporated in vacuo, the remaining residue was dissolved in 2 mL of CH_2Cl_2, and the solution was chromatographed on Al_2O_3 (basic, activity grade III). With CH_2Cl_2/hexane (5:1) a yellow fraction was eluted, which was brought to dryness in vacuo. The yellow solid (L = P*i*Pr$_3$, As*i*Pr$_3$) or light brown solid (L = Sb*i*Pr$_3$) was washed twice with 5 mL portions of hexane and dried: yield 46% for **42**, 49% for **43**, and 54% for **44**. The products were identified by comparing the NMR spectroscopic data with those of authentic samples.[9,23]

Preparation of [(η^6-mes)OsCl(=CPh_2)(PPh_3)]PF_6 (45). A solution of **28** (88 mg, 0.12 mmol) and PPh_3 (66 mg, 0.25 mmol) in 15 mL of THF was treated at −78 °C with a solution of $AgPF_6$ (61 mg, 0.24 mmol) in 5 mL of THF. After the reaction mixture was warmed to room temperature, it was filtered to remove the precipitate of AgCl. The filtrate was brought to dryness in vacuo, and the greenish oil was dissolved in 1.0 mL of CH_2Cl_2. The solution was filtered with Celite and then concentrated in vacuo to ca. 2 mL. After the solution was layered with 15 mL of hexane, a dark green solid precipitated. The formation of the product was facilitated by irradiation of the mixture in an ultrasonic bath. The green solid was separated from the mother liquor, washed twice with 5 mL portions of hexane, and dried: yield 212 mg (96%); mp 136 °C dec; Λ 67 cm^2 Ω^{-1} mol^{-1}. MS (FAB): *m*/*z* 775 ($M^+ + 1$). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.52−7.41 (m, 15 H, C−C_6H_5, P−C_6H_5), 7.09−7.03 (m, 10 H, C−C_6H_5, P−C_6H_5), 5.44 (s, 3 H, CH of mes), 2.07 (s, 9 H, CH_3 of mes). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): δ 292.3 [d, *J*(P,C) = 11.3 Hz, Os=C], 165.3 (s, *ipso*-C of C−C_6H_5), 134.2 [d, *J*(P,C) = 37.0 Hz, *ipso*-C of P−C_6H_5], 132.7 (s, *para*-C of C−C_6H_5), 131.4 [d, *J*(P,C) = 15.3 Hz, *ortho*-C of P−C_6H_5], 130.2, 127.4 (both s, *ortho*- and *meta*-C of C−C_6H_5), 129.6 (br s, *para*-C of P−C_6H_5), 128.8 [d, *J*(P,C) = 10.6 Hz, *meta*-C of P−C_6H_5], 121.6 [d, *J*(P,C) = 2.8 Hz, *C*CH_3 of mes], 87.3 [d, *J*(P,C) = 3.2 Hz, CH of mes], 18.5 (s, C*C*H_3 of mes). ^{31}P NMR (CD_2Cl_2, 81.0 MHz): δ 0.4 (s, PPh_3), −144.1 [sept, *J*(P,F) = 712.6 Hz, PF_6^-]. Anal. Calcd for $C_{40}H_{37}ClF_6OsP_2$ (919.3): C, 52.26; H, 4.06. Found: C, 52.19; H, 4.23.

Preparation of [(η^6-mes)OsCl{=C(*p*-C_6H_4Me)$_2$}(PPh_3)]PF_6 (46). This compound was prepared as described for **45**, from **29** (63 mg, 0.11 mmol), PPh_3 (31 mg, 0.12 mmol), and $AgPF_6$ (28 mg, 0.11 mmol). Green solid: yield 97 mg (93%), mp 151 °C dec; Λ 71 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.62−6.81 (m, 23 H, C_6H_5 and C_6H_4), 5.38 (s, 3 H, CH of mes), 2.23 (s, 6 H, $C_6H_4CH_3$), 2.04 (s, 9 H, CH_3 of mes).

^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ 291.2 [d, J(P,C) = 11.4 Hz, Os=C], 162.2 (br s, *ipso*-C of C_6H_4), 144.4 (s, *para*-C of C_6H_4), 134.6 [d, J(P,C) = 41.2 Hz, *ipso*-C of C_6H_5], 133.9 [d, J(P,C) = 15.3 Hz, *ortho*-C of C_6H_5], 131.3 (br s, *para*-C of C_6H_5), 131.0, 128.1 (both s, *ortho*- and *meta*-C of C_6H_4), 129.5 [d, J(P,C) = 8.3 Hz, *meta*-C of C_6H_5], 120.2 [d, J(P,C) = 2.1 Hz, CCH_3 of mes], 86.1 [d, J(P,C) = 3.8 Hz, CH of mes], 21.7 (s, $C_6H_4CH_3$), 18.4 (s, CCH_3 of mes). ^{31}P NMR (CD_2Cl_2, 81.0 MHz): δ 0.1 (s, PPh_3), −143.8 [sept, J(P,F) = 712.1 Hz, PF_6^-]. Anal. Calcd for $C_{42}H_{41}ClF_6OsP_2$ (947.4): C, 53.25; H, 4.36. Found: C, 53.21; H, 4.62.

X-ray Structural Determination of Compounds 2, 28·1/2CH_2Cl_2, and 35. Single crystals of these compounds were grown by slow diffusion of pentane or hexane into a solution of **2**, **28**·1/2CH_2Cl_2, or **35** in CH_2Cl_2 at room temperature. The data were collected for **2** on a Rigaku AFC6R diffractometer, for **28**·1/2CH_2Cl_2 on a Enraf-Nonius CAD 4 diffractometer, and for **35** on a Stoe IPDS diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal data collection parameters are summarized in Table 1. The corresponding data for **15** and **45** have already been reported.[4] Intensity data were corrected by Lorentz and polarization effects, and empirical absorption corrections were applied. The structures were solved by direct methods (SHELXS-97).[32] Atomic coordinates and anisotropic displacement parameters were refined by full matrix least-squares against F_o^2 (SHELXL-97).[33] The asymmetric unit of **28**·1/2CH_2Cl_2 contains half a molecule of CH_2Cl_2, the carbon atom of which (C40) lies on a special position. The second half of the CH_2Cl_2 molecule was generated with the symmetry operation $-x+1, y, -z+1$. The methyne hydrogen atom H3 of the acetylacetonato ligand of **35** was found in a differential Fourier synthesis and refined isotropically. The positions of all other hydrogen atoms were calculated according to ideal geometry and refined using the riding method.

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Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **2**, **28**·1/2CH_2Cl_2, and **35**. This material is available free of charge via the Internet at http://pubs.acs.org.

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