Organometallics **2000,** *19,* 4687−4689

The First Areneosmium(II) Complexes with Diarylcarbenes as Ligands

Birgit Weberndörfer, Gerhard Henig, and Helmut Werner*

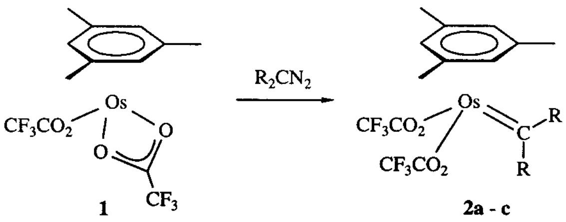
Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Received August 14, 2000

Summary: Using $[(\eta^6\text{-mes})Os(\kappa^1\text{-}O_2CCF_3)(\kappa^2\text{-}O_2CCF_3)]$ ***(1)*** *and diaryldiazomethanes as the starting materials, the half-sandwich-type carbeneosmium(II) complexes* $[(\eta^6\text{-mes})Os(\kappa^1\text{-}O_2CCF_3)_2({=}CR_2)]$ ***(2a−c****; R =* $p\text{-}C_6H_4X$ *with X = H, Me, Cl) were prepared. The dichloro derivatives* $[(\eta^6\text{-mes})OsCl_2({=}CR_2)]$ ***(3a,b)****, obtained from* ***2a,b*** *and* Me_3SiCl*, react with* PPh_3 *in the presence of* $AgPF_6$ *to form the cationic compounds* $[(\eta^6\text{-mes})OsCl({=}CR_2)(PPh_3)]PF_6$ ***(5a,b)****; moreover, the π-allyl complex* $[(\eta^6\text{-mes})OsBr(\eta^3\text{-}CH_2CHCPh_2)]$ ***(4)*** *was prepared from* ***2a*** *and* $CH_2{=}CHMgBr$*.*

In the context 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 observed that for the preparation of diarylcarbeneruthenium(II) compounds of the general composition $[(\eta^5\text{-}C_5H_5)RuX({=}CRR')(PPh_3)]$ (R = R′ = aryl; X = Cl, CH_3CO_2) the use of the acetato derivative $[(\eta^5\text{-}C_5H_5)Ru(\kappa^2\text{-}O_2CCH_3)(PPh_3)]$ as the starting material is the method of choice. It reacts with diaryldiazomethanes in toluene at room temperature via elimination of N_2 to give the compounds $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-}O_2CCH_3)({=}CRR')(PPh_3)]$, which upon treatment with $[Et_3NH]Cl$ are converted into the more stable chloro derivatives $[(\eta^5\text{-}C_5H_5)RuCl({=}CRR')(PPh_3)]$.[1] By taking into consideration that attempts to obtain half-sandwich-type carbeneosmium(II) complexes $[(\eta^6\text{-mes})OsCl_2({=}CRR')]$ from $[(\eta^6\text{-mes})OsCl_2]_n$ (mes = 1,3,5-$C_6H_3Me_3$) and diazomethanes $RR'CN_2$ failed,[2] we decided to apply the corresponding bis(trifluoroacetate) **1** as the precursor. From previous work it was known that compound **1** (which was prepared from $[(\eta^6\text{-mes})OsCl_2]_n$ and 2*n* equiv of CF_3CO_2Ag) reacts with CO and various phosphines to give the corresponding 1:1 adducts $[(\eta^6\text{-mes})Os(\kappa^1\text{-}O_2CCF_3)_2(L)]$, thereby converting one of the trifluoracetato ligands from a κ^2- to a κ^1-bonding mode.[3]

Scheme 1



1

2a - c

	R
a	C_6H_5
b	$p\text{-}C_6H_4Me$
c	$p\text{-}C_6H_4Cl$

We have now discovered (see Scheme 1) that a similar reaction of **1** takes place with diaryldiazomethanes. Upon treatment of a solution of **1** in benzene with a solution of R_2CN_2 in the same solvent at room temperature, a rapid evolution of gas (N_2), accompanied by a change of color from brown to green, occurred. Removal of the solvent and recrystallization of the residue from toluene−hexane (1:20) gave dark green or olive green, only moderately air-sensitive solids $[(\eta^6\text{-mes})Os(\kappa^1\text{-}O_2CCF_3)_2({=}CR_2)]$ (**2a−c**) in good to excellent yield.[4] The most typical spectroscopic feature of **2a−c** is the signal for the carbene carbon atom in the ^{13}C NMR spectra at δ 306−310, which is considerably shifted to lower field compared with $[(\eta^6\text{-mes})OsPh_2\{{=}C(NHMe)Ph\}]$ (δ 222).[5] For the ^{13}C nuclei of the aryl groups of **2a−c** only a single set of signals is observed, indicating that at room temperature the rotation around the Os−C(carbene) bond is not hindered on the NMR time scale.[6]

The X-ray crystal structure analysis of **2b** (Figure 1)[7] confirms the anticipated piano-stool configuration of the molecule. 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)[8] and in the six-coordinate osmium(II) complexes [OsHCl(=CHR)-

---

(1) Braun, T.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1995**, *117*, 7291−7292.

(2) Henig, G. Dissertation, Universität Würzburg, 1997.

(3) Werner, H.; Stahl, S.; Kohlmann, W. *J. Organomet. Chem.* **1991**, *409*, 285−298.

(4) **2a**: yield 91%, dark green solid, mp 89 °C dec. **2b**: yield 71%, olive green solid, mp 107 °C dec. **2c**: yield 58%, olive green solid, mp 118 °C dec. **3a**: yield 79%, olive green solid, mp 126 °C dec. **3b**: yield 87%, olive green solid, mp 153 °C dec. **4**: yield 61%, yellow solid, mp 94 °C dec. **5a**: yield 96%, dark green solid, mp 136 °C dec, Λ (CH_3NO_2) 67 $cm^2\ \Omega^{-1}\ mol^{-1}$. **5b**: yield 93%, dark green solid, mp 151 °C dec, Λ (CH_3NO_2) 71 $cm^2\ \Omega^{-1}\ mol^{-1}$.

(5) Werner, H.; Wecker, U.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1994**, *469*, 205−212.

(6) Selected spectroscopic data for **2a−c**, **3a**,**b**, **4**, and **5a**,**b** (omitting the ^1H and ^{13}C NMR data for the mesitylene ligand and the aryl groups as well as the ^{19}F and ^{31}P NMR data for the PF_6 anion) are as follows. **2a**: ^{13}C NMR (CD_2Cl_2, 50.3 MHz) δ 310.3 (s, Os=C), 161.7 (q, *J*(FC) = 36.9 Hz, CF_3CO_2), 114.3 (q, *J*(FC) = 290.7 Hz, CF_3CO_2); ^{19}F NMR (CD_2Cl_2, 188.3 MHz) δ −73.4 (s). **2b**: ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 307.9 (s, Os=C), 161.9 (q, *J*(FC) = 36.9 Hz, CF_3CO_2), 114.6 (q, *J*(FC) = 291.1 Hz, CF_3CO_2); ^{19}F NMR (CD_2Cl_2, 376.5 MHz) δ −75.3 (s). **2c**: ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 305.9 (s, Os=C), 162.1 (q, *J*(FC) = 37.2 Hz, CF_3CO_2), 114.5 (q, *J*(FC) = 290.7 Hz, CF_3CO_2); ^{19}F NMR (CD_2Cl_2, 376.5 MHz) δ −75.2 (s). **3a**: ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 299.2 (s, Os=C). **3b**: ^{13}C NMR (CD_2Cl_2, 50.3 MHz) δ 302.8 (s, Os=C). **4**: ^1H NMR (C_6D_6, 400 MHz) δ 5.00 (dd, *J*(HH) = 8.8 and 6.7 Hz, 1H, Ph_2CCHCH_2), 2.75 (dd, *J*(HH) = 6.7 and 1.5 Hz, 1H, Ph_2CCHCH_2), 2.42 (dd, *J*(HH) = 8.8 and 1.5 Hz, 1H, Ph_2CCHCH_2); ^{13}C NMR (C_6D_6, 100.6 MHz) δ 74.5 (s, CH_2CHCPh_2), 66.1 (s, CH_2CHCPh_2), 33.8 (s, CH_2CHCPh_2). **5a**: ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 292.3 (d, *J*(PC) = 11.3 Hz, Os=C). **5b**: ^{13}C NMR (CD_2Cl_2, 50.3 MHz) δ 291.2 (d, *J*(PC) = 11.4 Hz, Os=C).

10.1021/om0007062 CCC: $19.00
Publication on Web 10/21/2000

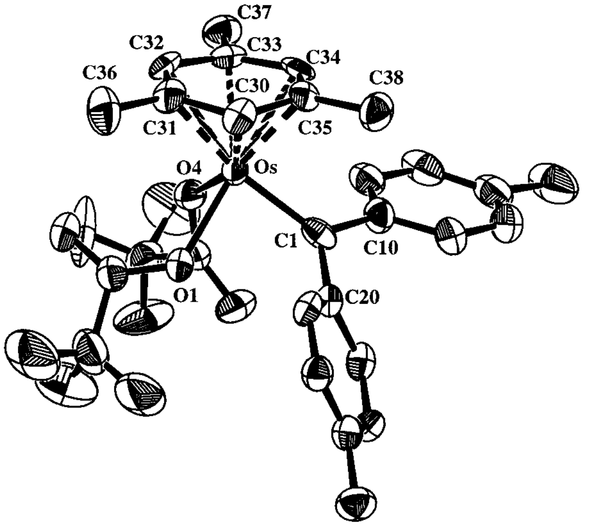


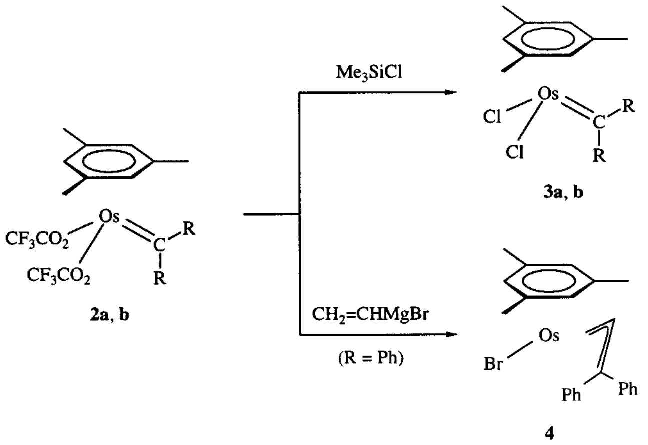
Figure 1. ORTEP diagram of compound **2b**. Selected bond distances (Å) and angles (deg): Os−O1, 2.108(4); Os−O4, 2.096(4); Os−C1, 1.957(7); Os−C30, 2.197(6); Os−C31, 2.328(6); Os−C32, 2.342(6); Os−C33, 2.207(6); Os−C34, 2.214(5); Os−C35, 2.265(5); C1−Os−O1, 85.0(2); C1−Os−O4, 95.1(2); O1−Os−O2, 81.8(2).

(CO)(P*i*Pr$_3$)$_2$] (R = CO$_2$Et: 1.949(2) Å; R = SiMe$_3$: 1.965(5) Å) and [OsCl$_2$(=CHPh)(CO)(P*i*Pr$_3$)$_2$] (1.95(2) Å);[9] it is, however, slightly shorter than in the above-mentioned species [(η^6-mes)OsPh$_2${=C(NHMe)Ph}] (1.992(5) Å) with a Fischer-type carbene ligand.[5] The two bond angles C1−Os−O1 and C1−Os−O4 differ by about 10°, which is presumably due to steric hindrance between one of the tolyl rings and the mesitylene unit.

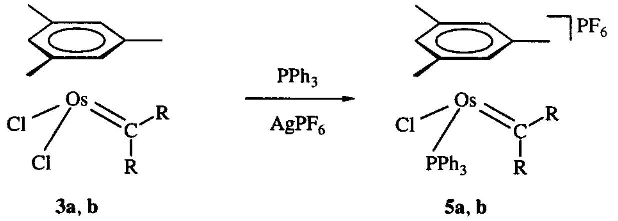
Treatment of **2a** or **2b** with a 3-fold excess of Me$_3$SiCl in CH$_2$Cl$_2$ at −78 °C results in a gradual change of color and affords after warming of the solution to room temperature, evaporation of the solvent, and recrystallization of the residue from toluene−hexane (1:2) the dichloro derivatives **3a** and **3b** in, respectively, 79% and 87% yield (Scheme 2). The ^{13}C NMR spectra of **3a** and **3b** display the carbene carbon resonance at δ 299.2 (**3a**) and 302.8 (**3b**) and thus at somewhat higher field compared with the CF$_3$CO$_2$ analogues.

The reaction of **2a** with the vinyl Grignard reagent CH$_2$=CHMgBr leads, in THF at low temperature, to the displacement of both trifluoracetate groups and to the formation of the π-allyl complex **4**, containing an unsymmetrical 1,1-diphenylallyl ligand. It is conceivable that a carbene(η^1-vinyl)metal species is formed as an intermediate, which by intramolecular C−C coupling rearranges to the final product. An alternative pathway, addition of the C-nucleophile to the carbene carbon followed by elimination of CF$_3$CO$_2^-$ with concomitant η^1/η^3 allyl rearrangment, could also be considered. Although on the basis of the ^{1}H and ^{13}C NMR data it cannot be decided whether the CH$_2$CHCPh$_2$ ligand of **4** is linked in *exo* or *endo* position to the (η^6-mes)OsBr fragment, there is no doubt that in contrast with the cyclopentadienylruthenium compounds [(η^5-C$_5$H$_5$)Ru(η^3-CH$_2$CHCR$_2$)(PPh$_3$)] (R = *p*-C$_6$H$_4$X)[1] only one isomer is present. In analogy with the structurally characterized 2-methylallyl complex [(η^6-mes)OsCl(η^3-CH$_2$CMeCH$_2$)][10] we assume that the *exo* isomer is thermodynamically preferred.

Scheme 2



Scheme 3



By attempting to further modify the coordination sphere of osmium(II) in the half-sandwich-type compounds [(η^6-mes)OsXY(=CR$_2$)], we also prepared cationic species via displacement of one of the chloro ligands in **3a**,**b** by triphenylphosphine. The PF$_6$ salts **5a**,**b** (Scheme 3) were obtained upon treatment of a solution of **3a**,**b** in THF with PPh$_3$ in the presence of AgPF$_6$ at −78 °C. After separation of AgCl, removal of the solvent, and recrystallization from CH$_2$Cl$_2$−hexane (1:7.5) dark green solids were isolated; they were characterized by elemental analysis, conductivity measurements, and spectroscopic techniques.

The molecular structure of the cation of **5b** is shown in Figure 2.[11] While the Os−C(ring) distances in the half-sandwich-type cation are somewhat longer than in the neutral complex **2b**, the Os−C1 distance of 1.93(1) Å is nearly identical to that in **2b**. Two of the bond

---

(7) Crystal data for **2b**: monoclinic, $P2_1/c$ (No. 14), $a = 11.989(1)$ Å, $b = 11.998(1)$ Å, $c = 19.542(2)$ Å, $\beta = 106.35(1)°$, $V = 2695.1(4)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.801$ g cm^{-3}, $T = 173(2)$ K, μ(Mo Kα) = 4.814 cm^{-1}; data collected on a Stoe IPDS diffractometer using Φ scan mode ($2\theta_{\max} = 54.12°$); 25 917 reflections scanned, 5880 unique, 3482 observed ($I > 2\sigma(I)$); 385 parameters refined to give $R = 3.72\%$ and $R_w = 7.80\%$ with a reflex-parameter ratio of 15.3 and a residual electron density +0.761/−1.442 e Å^{-3}.

(8) (a) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939−5940. (b) Roper, W. R. *J. Organomet. Chem.* **1986**, *300*, 167−190.

(9) Werner, H.; Stüer, W.; Wolf, J.; Laubender, M.; Weberndörfer, B.; Herbst-Irmer, C.; Lehmann, C. *Eur. J. Inorg. Chem.* **1999**, 1889−1897.

(10) Wecker, U.; Werner, H.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1994**, *127*, 1021−1029.

(11) Crystal data for **5b**·0.85 CH$_2$Cl$_2$: monoclinic, $P2_1$ (No. 4), $a = 9.876(1)$ Å, $b = 22.627(2)$ Å, $c = 10.416(1)$ Å, $\beta = 117.63(1)°$, $V = 2062.2(4)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.642$ g cm^{-3}, $T = 193(2)$ K, μ(Mo Kα) = 4.814 cm^{-1}; data collected on a Stoe IPDS diffractometer using Φ scan mode ($2\theta_{\max} = 50.02°$); 12 498 reflections scanned, 6665 unique, 5001 observed ($I > 2\sigma(I)$); extinction parameter 0.0010(2), Flack parameter −0.024(10), 503 parameters refined to give $R = 4.26\%$ and $R_w = 6.96\%$ with a reflex-parameter ratio of 13.2 and a residual electron density +1.303/−1.039 e Å^{-3}.

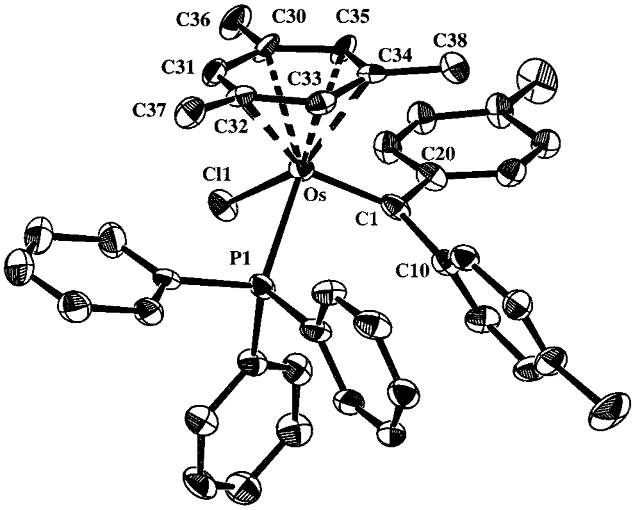


Figure 2. ORTEP diagram of the cation of **5b**. Selected bond distances (Å) and angles (deg): Os−P1, 2.377(2); Os−C1, 2.384(2); Os−C1, 1.93(1); Os−C30, 2.305(9); Os−C31, 2.35(1); Os−C32, 2.40(1); Os−C33, 2.26(1); Os−C34, 2.325(10); Os−C35, 2.27(1); C1−Os−P1, 93.4(3); C1−Os−C1, 98.1(4); P1−Os−C1, 81.54(9).

angles of the $OsL^1L^2L^3$ fragment, C1−Os−P1 (93.4(3)°) and C1−Os−C1 (98.1(4)°), are considerably larger than the third one (P1−Os−C1 = 81.54(9)°), which we assume is due to the steric demand of the carbene ligand.

In conclusion, we have shown that by using **1** as the starting material the preparation of areneosmium(II) complexes with diarylcarbene ligands can be achieved. Moreover, from the neutral precursors **3a**,**b** related cationic species **5a**,**b** can be generated. Although various osmium(0) and osmium(II) compounds containing an $Os{=}CR_2$ unit are already known,[8,9,12,13] to the best of our knowledge **2a**−**c**, **3a**,**b**, and **5a**,**b** are the first half-sandwich-type osmium complexes with a non-Fischer-type carbene ligand.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (Grant No. SFB 347), the Fonds der Chemischen Industrie, and the BASF AG.

Supporting Information Available: A table with the elemental analysis of compounds **2a**−**c**, **3a**,**b**, **4**, and **5a**,**b** as well as fully labeled diagrams and tables of crystallographic data, data collection, and solution and refinement details, positional and thermal parameters, and both distances and angles for **2b** and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0007062

---

(12) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293−1326.

(13) (a) Werner, H.; Weber, B.; Nürnberg, O.; Wolf, J. *Angew. Chem.* **1992**, *104*, 1105−1107; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1025−1026. (b) Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 4258−4265. (c) Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935−7942.