examples of this "arm-off" process. That such a process is tenable is further supported by our isolation of Rh(η^6-$PhBPh_3$)(η^2-triphos) as a ground-state "arm-off" species. Finally, the fact that $RhX(C_2H_4)$(triphos) is fluxional (by an "arm-off" mechanism) for X = Cl but static for X = H, C_2H_5 indicates that the resulting 16-electron η^2-triphos species are stabilized by π-donation from the chloride ligand. The broad conclusion from all of these results is the reminder that the chelate effect enhances thermodynamic stability of coordinate bonds but that such bonds may nevertheless be kinetically labile.[15]

Acknowledgment. This work was supported by the National Science Foundation. We thank Johnson Matthey for material support.

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A New Family of (Arene)osmium(0) and -osmium(II) Complexes

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The arene carbonyl complex [(mes)$OsCl_2$(CO)] (**3**), which is obtained from [(mes)$OsCl_2$]$_n$ (**1**) and CO in CH_2Cl_2, reacts with CH_3MgI and CH_3Li to give the monomethyl- and dimethylosmium(II) compounds [(mes)$OsCH_3$(CO)I] (**4**) and [(mes)Os$(CH_3)_2$(CO)] (**5**) in good yields. Treatment of **5** with [CPh_3]PF_6 leads to the formation of [(mes)OsH(C_2H_4)(CO)]PF_6 (**6**), which by deprotonation with NaH gives the osmium(0) complex [(mes)Os(C_2H_4)(CO)] (**7**). With [(mes)Os$(CD_3)_2$(CO)] (**5**-d_6) as starting material, the deuterated compound [(mes)Os(C_2D_4)(CO)] (**7**-d_4) has similarly been prepared, which proves that neither the solvent nor the particular reagent is involved in the two reaction steps. The synthesis of the dihydrido complexes [(mes)OsH_2(CO)] (**10**), [(C_6H_6)OsH_2(CO)] (**13**), and [(C_6Me_6)RuH_2(CO)] (**14**) has been achieved by treatment of the corresponding dichloro or diiodo derivatives with sodium in liquid ammonia in presence of *tert*-butyl alcohol as a proton source. Reaction of **10** with HBF_4 in CH_2Cl_2 produces the BF_4 salt of the [(mes)OsH_3(CO)]$^+$ cation (**15**), which reacts with CO to give [(mes)OsH$(CO)_2$]BF_4 (**16**). Deprotonation of **16** with NaH or $NaNH_2$ in THF leads to the formation of the dicarbonyl compound [(mes)Os$(CO)_2$] (**17**). The related olefin osmium(0) complexes [(mes)Os$(C_2H_4)_2$] (**18**) and [(mes)Os(C_7H_8)] (**19**) have been prepared from **1** and ethylene or norbornadiene, respectively, in presence of Na_2CO_3 and ethanol. By use of **3** and **4** as starting materials, the monocarbonylosmium(II) compounds [(mes)OsH(CO)Cl] (**9**) and [(mes)$OsCH_3$(CO)H] (**8**) have also been synthesized.

Introduction

Following our original work on (arene)ruthenium(0) and -osmium(0) complexes of the general type [(C_6R_6)ML_2] (L = PR_3 or P$(OR)_3$) and [(C_6R_6)M(PR_3)L] (L = P$(OR)_3$, CO, C_2H_4, etc.), which proved to be strong nucleophiles,[1,2] we have recently also prepared a variety of dihydrido- and dialkylruthenium(II) and -osmium(II) compounds [(C_6R_6)MX_2(PR_3)] (X = H, alkyl)[3,4] to compare their reactivities with those of the corresponding metal(0) derivatives. During attempts to insert unsaturated molecules such as CO, CO_2, or C_2H_4 into the Ru–H bonds of the (arene)ruthenium complexes [(C_6R_6)RuH_2(PR_3)] (PR_3 = PMe_3, P-*i*-Pr_3) in benzene or toluene as the solvent, we observed that under photolytic conditions H_2 is eliminated and the aryl hydrido compounds [(C_6R_6)RuH(C_6H_4Y)(PR_3)] (Y = H, Me) are formed.[5] This result was reminiscent of the pioneering work by Bergman[6] and Graham,[7] who showed that 16-electron fragments of the general type [(C_5R_5)Ir(L)] (R = H, Me; L = PR_3, CO) are able to react with aromatic as well as with aliphatic hydrocarbons by oxidative addition. As according to Bergman there were no severe conditions necessary to abstract H_2 from [(C_5Me_5)IrH_2(PMe_3)][8] and as this result was in full agreement with our own studies on the behavior of [(C_6R_6)RuH_2(PR_3)],[5] we were very surprised to learn that both under thermal and photolytic conditions the analogous osmium dihydride [(C_6H_6)OsH_2(P-*i*-Pr_3)] was completely inert. Even prolonged irradiation with UV light of 2537 Å in benzene or toluene did not lead to the for-

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mation of the expected arylhydridoosmium derivatives.[9]

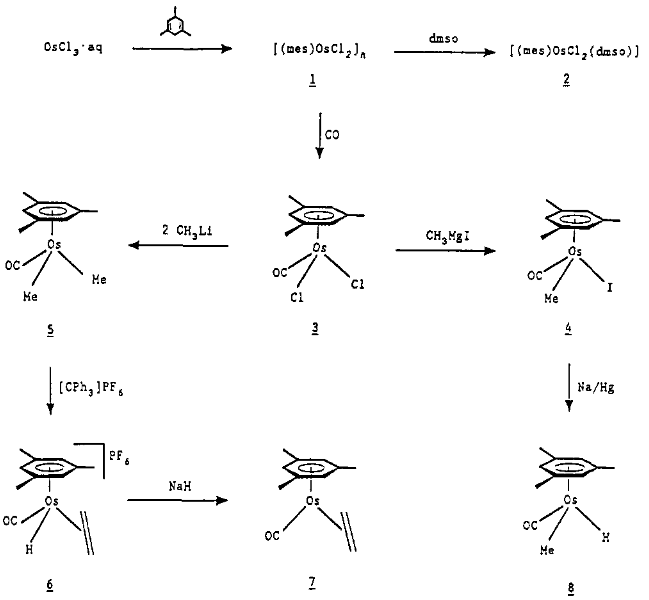
To explain the inert character of [$(C_6H_6)OsH_2(P$-*i*-$Pr_3)$], we assumed that trialkylphosphine, which is known to be a good donor ligand, increases the electron density at the metal center and thus strengthens the Os-H bonds. We concluded that P-*i*-Pr_3 should therefore be substituted by a weaker donor molecule such as CO, C_2H_4, etc. Thus, the synthesis of an (arene)carbonyldihydridoosmium complex was a main goal of the present work. Furthermore, as we had shown that not only [$(C_6H_6)OsH_2(P$-*i*-$Pr_3)$] but also [$(C_6H_6)Os(CO)(P$-*i*-$Pr_3)$] was unreactive on photolysis,[9] the second objective was the preparation of an arene osmium(0) dicarbonyl and/or of related compounds [$(C_6R_6)OsL_2$] and [$(C_6R_6)OsLL'$] *without* phosphine ligands. In this paper we describe the results of investigations that have led to a new family of (arene)carbonyl and (olefin)osmium(0) and -osmium(II) complexes.

Results

[(mes)Os(CO)(C_2H_4)]. The main steps of the synthesis of the carbonyl(ethylene)osmium(0) complex follow the route that we have used for the corresponding benzene derivative [$(C_6H_6)Os(CO)(C_2H_4)$].[10] The starting material is (mesitylene)osmium dichloride (1), which is obtained in virtually quantitative yield from $OsCl_3 \cdot 3H_2O$ and 1,3,5-trimethylcyclohexa-1,4-diene in ethanol under reflux. The same reaction was previously carried out also by Bennett et al.,[11] who isolated a product with the analytical composition [$(mes)_3Os_4Cl_9$]. [We have been informed by Prof. M. A. Bennett (private communication, Jan 1990) that they have occasionally obtained [$(mes)OsCl_2]_2$ instead of the tetranuclear compound. It mainly depends on the starting material used for the reaction with 1,3,5-trimethylcyclohexa-1,4-diene, which they prepared by heating OsO_4 with concentrated HCl and subsequent evaporation in a vacuum.] Complex 1 is a yellow-brown microcrystalline solid that is almost insoluble in all common organic solvents. It dissolves very slowly in dimethyl sulfoxide (DMSO) to give a brownish yellow solution from which a yellow solid analyzing as [$(mes)OsCl_2(DMSO)$] (2) is isolated. The ^1H NMR spectrum of 2 (in DMSO-d_6) shows two singlets at δ 5.74 and 2.22 in the intensity ratio of 3:9, which correspond to the CH and CH_3 protons of the mesitylene unit. The NMR data are in full agreement with those reported by Bennett et al. for [$(mes)_3Os_4Cl_9$],[11] and thus we assume that in both cases the complex [(mes)$OsCl_2$(DMSO-d_6)] is formed. Owing to the chemical shift of the $(CH_3)_2SO$ signal in the ^{13}C NMR spectrum of 2, we conclude that the dimethyl sulfoxide is S bonded.[12] Complex 1 is probably polymeric, having a similar structure to [$(C_6H_6)RuCl_2]_n$, which on treatment with DMSO also produces a monomeric species, [$(C_6H_6)RuCl_2(DMSO)$].[13]

The chloro bridges in 1 can be split not only by DMSO but also by carbon monoxide to give [(mes)Os(CO)Cl_2] as an orange, rather air-stable solid (Scheme I). The formation of 3 is significantly faster than that of the corresponding iodo derivative [$(C_6H_6)Os(CO)I_2$],[10] which in agreement with previous observations[14] indicates that fragmentation of [$(arene)OsX_2]_n$ compounds into monomeric species by attack of nucleophiles proceeds more smoothly for X = Cl than for X = I.

Scheme I



Substitution of the chloro ligands in 3 by methyl can be done in two ways. Whereas with CH_3MgI in ether the monosubstituted product [(mes)$OsCH_3$(CO)I] (4) is formed, treatment of 3 with excess methyllithium in benzene/ether gives the dimethylosmium complex [(mes)$Os(CH_3)_2$(CO)] (5). The IR spectrum of this yellow air-sensitive solid shows a strong CO stretching frequency at 1910 cm^{-1}, which appears at lower wave numbers than that of [$(C_6H_6)Os(CH_3)_2(CO)$],[10] in full agreement with the greater donor strength of mesitylene compared with benzene.

Reaction of 5 with [CPh_3]PF_6 proceeds at ambient temperature in dichloromethane to give the carbonyl ethylene hydrido complex [(mes)OsH(C_2H_4)(CO)]PF_6 (6) in ca. 70% yield. In accordance with the results of our previous investigations,[3b,d] we propose that the trityl cation abstracts a hydride from one of the CH_3 groups to give a [Os(=CH_2)CH_3] intermediate. This can then rearrange by CH_3 migration (and probably not by CH_2 insertion[15]) to form the corresponding ethylosmium compound from which 6 is obtained by β-hydride elimination. We note that the presently accepted concepts regarding the mechanism of the Fischer-Tropsch process include the assumption that primary C-C bond formation on the surface of the catalyst occurs by combination of a CH_3 either with a CO group or with a CH_2 unit generated in the hydrogenation step.[16] In the mononuclear species formed in the reaction of [(arene)$Os(CH_3)_2$(CO)] with [CPh_3]PF_6, obviously the migration of a CH_3 group to a CH_2 instead of a CO ligand seems to be preferred.

In the final step (see Scheme I), deprotonation of 6 with NaH in tetrahydrofuran leads to the formation of [(mes)Os(C_2H_4)(CO)] (7), which is one of the rare examples of a half-sandwich type complex [(arene)MLL'] (M = Fe, Ru, Os) containing besides the arene two *monodentate* π-acceptor ligands. According to the increased electron

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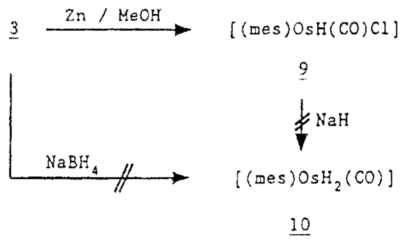
Scheme II



Scheme III

$$[(ar)MX_2(CO)] \xrightarrow[t\text{-BuOH}]{Na/NH_3} [(ar)MH_2(CO)]$$

3 X = Cl, ar = mes, M = Os 10
11 X = I, ar = C_6H_6, M = Os 13
12 X = Cl, ar = C_6Me_6, M = Ru 14

density at the metal center compared with the cation of **6**, the ν(CO) band in the IR spectrum of **7** is found at 1922 cm^{-1} (**6**, 2010 cm^{-1}) whereas in the ^{1}H NMR spectrum the signals of the CH and CH_3 protons are shifted upfield. We note that the stability of **7** both thermally as well as toward oxidation is significantly higher than that of $[(C_6H_6)Os(C_2H_4)(PMe_3)]$[1e] and [(mes)Os(CO)($PMe_3$)],[17] which is due to the electron-withdrawing ability of the two π-acceptor ligands.

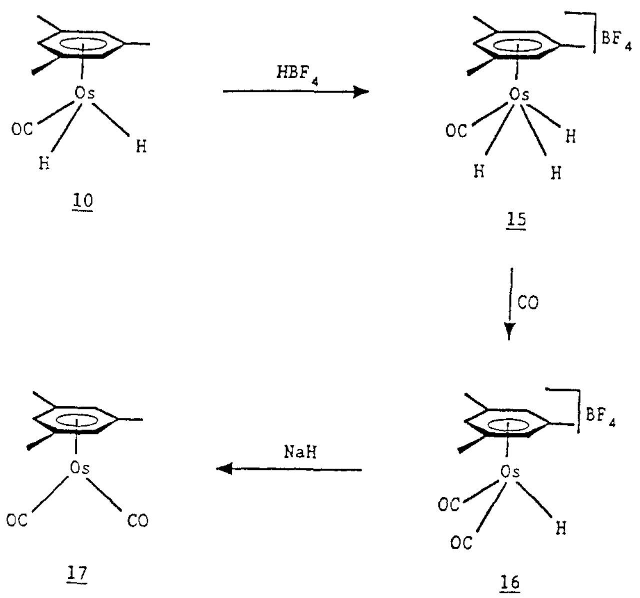
With regard to the mechanism of formation of **7** from **5** we have proved that [(mes)Os(CD_3)$_2$(CO)] (**5**-d_6), prepared from **3** and CD_3Li, reacts with $[CPh_3]PF_6$ to give [(mes)OsD(C_2D_4)(CO)]PF_6 (**6**-d_5), and this on treatment with NaH produces [(mes)Os(C_2D_4)(CO)] (**7**-d_4). Therefore neither the solvent nor the particular reagent is involved in the two steps.

[(mes)OsCH$_3$(CO)H]. The reaction of **4** with Na/Hg in THF/EtOH leads almost quantitatively to the formation of [(mes)OsCH$_3$(CO)H] (**8**). Recently, by use of $NaBH_4$ or $LiAlH_4$ as a hydride source, the related compounds $[(C_6H_6)OsCH_3(L)H]$ (L = P-*i*-Pr$_3$, P(OMe)$_3$, P(O-*i*-Pr)$_3$) have also been prepared.[18] It should be mentioned that the hydrido methyl complex **8**, which is isolated as a yellow solid, is the photoproduct both from [(mes)OsH$_2$(CO)] (**10**) and [(mes)Os(CO)$_2$] (**17**) in CH_4 matrices.[19]

[(mes)OsH$_2$(CO)]. Preparative pathways leading to dihydrido complexes of the general type [(arene)MH$_2$(CO)] (M = Ru, Os) have to the best of our knowledge so far not been described. Recently, it was mentioned by Graham[20] that the compound $[(C_6Me_6)OsH_2(CO)]$ had been used for C–H activation, but no details of the synthesis were given.

The method we[3a,13] as well as Maitlis and co-workers[21] employed to prepare [(arene)MH$_2$(PR$_3$)], namely, the reaction of [(arene)MX$_2$(PR$_3$)] with $NaBH_4$, $LiAlH_4$, or Red-al, does not succeed for [(mes)OsH$_2$(CO)] (**10**). With **3** as starting material and $NaBH_4$ or $LiAlH_4$ as a hydride donor, only decomposition products have been obtained. Reaction of **3** with zinc in methanol at room temperature gives the monohydride [(mes)OsH(CO)Cl] (**9**), but treatment of this compound with NaH or $NaBH_4$ also does not lead to the formation of **10** (Scheme II).

Scheme IV



The successful route to the carbonyl dihydrido complex **10** follows the procedure of the Birch reduction of organic substrates.[22] The dichloro compound **3** reacts with Na in liquid ammonia in presence of *tert*-butyl alcohol as a proton source to give **10** in ca. 50% yield. The synthesis of the (benzene)osmium complex $[(C_6H_6)OsH_2(CO)]$ (**13**) occurs analogously (Scheme III). In contrast, the (hexamethylbenzene)ruthenium compound $[(C_6Me_6)RuH_2(CO)]$ (**14**) has been isolated only in small quantities, which is probably due to the greater lability of the C_6Me_6–Ru compared with the C_6R_6–Os bond.

The carbonyl dihydrido complexes **10**, **13**, and **14** are white air-sensitive solids soluble in all common organic solvents. The decrease in the CO stretching frequency from **3** (1987 cm^{-1}) to **9** (1950 cm^{-1}) and further to **10** (1935 cm^{-1}) reflects the increasing Os–CO back-bonding, which is in accordance with the higher donor strength of hydride compared with chloride as ligand.

[(mes)Os(CO)$_2$]. The synthesis of the ruthenium compound $[(C_6Me_6)Ru(CO)_2]$, although in very low yield, had recently been achieved by reduction of $[(C_6Me_6)Ru(CO)_2Cl]PF_6$ with $NaC_{10}H_8$ in THF.[10b] The same procedure cannot be applied for [(mes)Os(CO)$_2$] (**17**) because the cation [(mes)Os(CO)$_2$Cl]$^+$ is not accessible from **3** and $AgPF_6$ under CO atmosphere. Also reduction of **1** with Na/Hg, zinc powder, activated magnesium, or $NaC_{10}H_8$ under CO does not lead to the formation of **17**.

The dicarbonyl complex can be prepared, however, on a rather unexpected route (Scheme IV). Like $[(C_6H_6)OsH_2(P\text{-}i\text{-}Pr_3)]$,[3c] the corresponding dihydrido compound **10** reacts with HBF_4 in dichloromethane at −78 °C to give [(mes)OsH$_3$(CO)]BF$_4$ (**15**) which according to preliminary T_1 measurements probably is a classical hydride.[23] On treatment of **15** with CO, the complex [(mes)OsH(CO)$_2$]BF$_4$ (**16**) is formed, which on reduction with NaH or $NaNH_2$ in THF affords **17**. The dicarbonyl, which has been isolated as a yellow solid, sublimes in vacuo and is significantly more stable than the related (hexamethylbenzene)iron and -ruthenium compounds $[(C_6Me_6)M(CO)_2]$ (M = Fe,[24] Ru[10b]). It is worth mentioning that in the IR spectrum of **17** the CO stretching frequencies (1978 and 1907 cm^{-1}, in hexane) are found at lower wavenumbers

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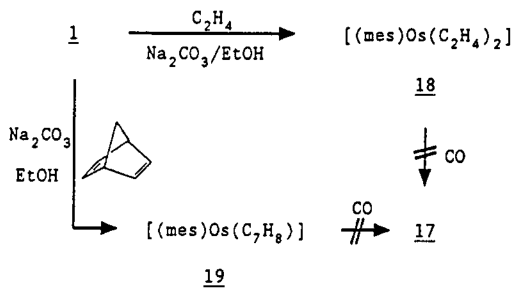
Scheme V



than in the structurally related iridium half-sandwich type compounds, [(C_5H_5)Ir(CO)$_2$][25] and [(C_5Me_5)Ir(CO)$_2$],[26] which points to a higher electron density at the osmium atom in the dicarbonyl complex.

[(mes)Os(C_2H_4)$_2$] and [(mes)Os(C_7H_8)]. As the parent compound 1 does not react with ethylene to produce [(mes)Os(C_2H_4)Cl_2], the preparation of [(mes)Os(C_2H_4)$_2$] (18) cannot follow the route developed for 17. Previously, Bennett and co-workers reported[27] that [(C_6Me_6)Ru(C_2H_4)$_2$] was synthesized in good yield from [(C_6Me_6)RuCl_2]$_2$ and ethylene in the presence of Na_2CO_3 and ethanol. This method is also suitable for 18 and [(mes)Os(C_7H_8)] (19, Scheme V). Both compounds have been isolated as yellow crystalline solids that are moderately air-stable and soluble in all common organic solvents. (Both complexes 18 and 19 have independently been prepared by Bennett et al. (Bennett, M. A., private communication).) As the ^1H NMR spectrum of 18 shows at room temperature two well-separated signals for the C_2H_4 protons at δ 2.04 and 0.94, we conclude that under these conditions the rotation of the olefin ligands around the Os–C_2H_4 axes is significantly hindered, in analogy to [(C_6Me_6)Ru(C_2H_4)$_2$][27] and in contrast to [(C_5H_5)Rh(C_2H_4)$_2$].[28] Neither 18 nor 19 react with CO by ligand displacement to give 17, and thus the stepwise synthesis shown in Scheme IV remains the method of choice for the elusive dicarbonyl complex.

Concluding Remarks

The work presented in this paper establishes a new family of (arene)osmium(0) and -osmium(II) complexes for which the foundation was led by the work of Bennett[11,27] and Maitlis[21] as well as by our own studies in this field.[1–5,10,14,18,29] The forecast that mesitylene as the arene ligand will stabilize molecules of the general type [(arene)MH_2(CO)], [(arene)M(CO)$_2$], [(arene)M(CO)(C_2H_4)], and [(arene)M(C_2H_4)$_2$] has been definitely fulfilled and confirms the trend already found in [(arene)M(CO)$_3$] (M = Cr, Mo, W) and [(arene)M(C_5H_5)]$^+$ (M = Fe, Ru) complexes. It is supposed that a corresponding series with C_6Me_6 as arene might afford even more stable derivatives, and thus the forthcoming results by Graham[20] have to be awaited.

The determining assumption for this work that the substitution of PR_3 in the well-known complexes [(arene)OsH_2(PR_3)], [(arene)Os(CO)(PR_3)], and [(arene)Os(C_2H_4)(PR_3)][1,3,5,14,18] by CO will lead to an increase in reactivity as far as C–H activation is concerned is certainly correct. The preliminary results obtained in close collaboration with the Perutz group[19] leave no doubt that the various carbonyl- and (ethylene)osmium complexes described in this paper are useful starting materials for photochemical reactions with alkanes, arenes, etc. At present it is hard to predict whether the new (arene)osmium compounds offer advantages over the well-established cyclopentadienyl and pentamethylcyclopentadienyl iridium complexes,[6–8] and thus work in this field will continue. From a preparative point of view, the synthetic route leading to the dicarbonyl 17 is particularly intriguing as it shows that the formation of an osmium(0) complex from an osmium(II) precursor is possible without a reducing agent such as Na/Hg, $NaC_{10}H_8$, etc. and might open the gate also to other CO-containing (arene)ruthenium(0) and -osmium(0) derivatives.

Experimental Section

All reactions were carried out under an atmosphere of argon by using Schlenk tube techniques. The starting materials [(C_6H_6)Os(CO)I_2] (11) and [(C_6Me_6)Ru(CO)Cl_2] (12) were prepared by published methods.[10b,29] The osmium trichloride was a gift from Degussa AG. NMR spectra were recorded on a JEOL FX 90 Q and a Bruker AC 200 instruments, IR spectra on a Perkin-Elmer 1420 infrared spectrophotometer, and mass spectra on a Varian MAT CH 7 instrument.

Preparation of [(mes)OsCl_2]$_n$ (1). A suspension of $OsCl_3\cdot 3H_2O$ (510 mg, 1.45 mmol) in 35 mL of ethanol was treated with 1,3,5-trimethylcyclohexa-1,4-diene and heated for 16 h under reflux. After cooling to room temperature, the suspension was concentrated to ca. 20 mL and stored for 2 h at 0 °C. The mother liquor was removed, and the solid residue was repeatedly washed with ether and dried in vacuo. A yellow-brown powder was obtained, yield 503 mg (91%). Anal. Calcd for $C_9H_{12}Cl_2Os$: C, 28.35; H, 3.17. Found: C, 28.44; H, 3.06.

Preparation of [(mes)OsCl_2(DMSO)] (2). A suspension of 1 (104 mg, 0.14 mmol for $n = 2$) in 6 mL of dichloromethane was treated with 0.5 mL of DMSO and stirred for 1 h at room temperature. The solution was filtered, the filtrate was concentrated to ca. 1–2 mL, and ether was added. A yellow precipitate was obtained which was filtered off, washed with ether and hexane, and dried in vacuo, yield 90 mg (72%). Anal. Calcd for $C_{11}H_{18}Cl_2OOsS$: C, 28.76; H, 3.95. Found: C, 28.73; H, 3.88. IR (KBr) ν(SO) 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.43 (s, $C_6H_3Me_3$), 3.18 (s, $OSMe_2$), 2.32 (s, $C_6H_3Me_3$); ^{13}C NMR ($CDCl_3$) δ 96.6 (CCH_3), 76.2 (CH), 42.4 ((CH_3)$_2$SO), 18.6 (CCH_3).

Preparation of [(mes)Os(CO)Cl_2] (3). A stream of CO was passed for 1 h through a suspension of 1 (680 mg, 0.89 mmol for $n = 2$) in 70 mL of dichloromethane. The solution was filtered, and the filtrate concentrated in vacuo to ca. 15 mL. After addition of 50 mL of ether, an orange precipitate was obtained which was washed with ether and dried in vacuo. The crude product was recrystallized from CH_2Cl_2/OEt_2 to give an orange-red microcrystalline solid, yield 600 mg (82%). Anal. Calcd for $C_{10}H_{12}Cl_2OOs$: C, 29.33; H, 2.96. Found: C, 28.91; H, 2.78. IR (KBr) ν(CO) 1987 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.47 (s, $C_6H_3Me_3$), 2.47 (s, $C_6H_3Me_3$).

Preparation of [(mes)OsCH_3(CO)I] (4). A suspension of 3 (102 mg, 0.25 mmol) in 5 mL of ether was treated at −78 °C with an equimolar amount of methylmagnesium iodide in ether. After warming to room temperature, the solution was stirred for 10 min, and the solvent removed in vacuo. The residue was extracted with 15 mL of benzene, the extract filtered, and the filtrate concentrated to ca. 2 mL. The concentrated solution was chromatographed on Al_2O_3 (neutral, activity grade V) by using benzene as an eluant. An orange-red fraction was separated which was concentrated in vacuo to ca. 1 mL. After addition of 10 mL of hexane, an orange precipitate was obtained which after decantation of the mother liquor was repeatedly washed with hexane and dried in vacuo, yield 65 mg (54%), mp 162 °C (dec). Anal. Calcd for $C_{11}H_{15}IOOs$: C, 27.51; H, 3.15. Found: C, 27.36; H, 3.12. MS (70 eV), m/z 482 (45, M$^+$), 467 (31, M$^+$ − CH_3), 454 (5,

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$M^+ - CO$), 439 (100, $M^+ - COCH_3$); IR (KBr) ν(CO) 1942 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.35 (s, $C_6\mathit{H}_3Me_3$), 1.89 (s, $C_6H_3\mathit{Me}_3$), 1.65 (s, $OsC\mathit{H}_3$).

Preparation of [(mes)Os(CH_3)$_2$(CO)] (5). A suspension of **3** (166 mg, 0.41 mmol) in 5 mL of benzene was treated dropwise at 0 °C with 1.3 mL of a 0.75 M solution of methyllithium in ether (0.98 mmol). After stirring for 15 min, a yellow-brown solution was obtained which was brought to dryness in vacuo. The residue was dissolved in 2 mL of benzene-hexane (1:1), and the solution was treated with ca. 100 mg of Al_2O_3 (to destroy the excess of MeLi) and then chromatographed on Al_2O_3 (neutral, activity grade III). With benzene/hexane (1:1) a yellow fraction was eluted from which after removing the solvent in vacuo a yellow microcrystalline powder was obtained, yield 107 mg (72%). Anal. Calcd for $C_{12}H_{18}OOs$: C, 39.12; H, 4.92. Found: C, 38.99; H, 5.00. MS (70 eV), *m/z* 370 (73, M^+), 355 (43, $M^+ - CH_3$), 327 (71, $M^+ - CH_3 - CO$); IR (KBr) ν(CO) 1910 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.30 (s, $C_6\mathit{H}_3Me_3$), 1.78 (s, $C_6H_3\mathit{Me}_3$), 0.72 (s, $Os(CH_3)_2$).

Preparation of [(mes)Os(CD_3)$_2$(CO)] (5-*d*$_6$) occurred analogously as described for **5**, using **3** (265 mg, 0.65 mmol) and 1.7 mL of a 0.96 M solution of CD_3Li in ether (obtained from CD_3I and lithium) as starting materials. After recrystallization from hexane a yellow microcrystalline solid was isolated, yield 125 mg (52%). Anal. Calcd for $C_{12}H_{12}D_6OOs$: C, 38.49; H + D, 6.45. Found: C, 38.46; H + D, 6.10. MS (70 eV), *m/z* 376 (67, M^+), 358 (37, $M^+ - CD_3$), 330 (63, $M^+ - CD_3 - CO$); IR (hexane) ν(CO) 1947 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.23 (s, $C_6\mathit{H}_3Me_3$), 1.74 (s, $C_6H_3\mathit{Me}_3$).

Preparation of [(mes)OsH(C_2H_4)(CO)]PF_6 (6). A solution of **5** (70 mg, 0.19 mmol) in 3 mL of ether was treated at –78 °C dropwise with a solution of [CPh_3]PF_6 (68.5 mg, 0.18 mmol) in 2 mL of dichloromethane. The solution was slowly warmed to room temperature and furthermore stirred for 30 min. After addition of 10 mL of ether a brownish precipitate was formed. The mother liquor was removed, and the solid residue was repeatedly washed with ether and dried in vacuo, yield 64 mg (71%). Anal. Calcd for $C_{12}H_{17}F_6OOsP$: C, 28.13; H, 3.34. Found: C, 28.35; H, 3.45. IR (KBr) ν(OsH) 2120, ν(CO) 2010 cm^{-1}; ^{1}H NMR (acetone-*d*$_6$) δ 6.87 (s, $C_6\mathit{H}_3Me_3$), 2.67 (s, $C_6H_3\mathit{Me}_3$), 2.2–3.0 (m, C_2H_4), –12.60 (s, OsH).

Preparation of [(mes)OsD(C_2D_4)(CO)]PF_6 (6-*d*$_5$) occurred analogously as described for **6**, using **5**-*d*$_6$ (115 mg, 0.31 mmol) and [CPh_3]PF_6 (114.4 mg, 0.29 mmol) as starting materials, yield 112 mg (70%). Anal. Calcd for $C_{12}H_{12}D_5F_6OOsP$: C, 27.85; H + D, 4.28. Found: C, 28.01; H + D, 4.34.

Preparation of [(mes)Os(C_2H_4)(CO)] (7). A solution of **6** (80 mg, 0.16 mmol) in 10 mL of tetrahydrofuran was treated under vigorous stirring with an excess of NaH (ca. 150 mg). After 20 min at room temperature, the solvent was removed, and the residue was extracted twice with 5 mL of benzene/hexane (1/1). The solution was filtered and brought to dryness in vacuo. After recrystallization from hexane at 25 to –78 °C a pale yellow crystalline solid was obtained, yield 49 mg (86%). Anal. Calcd for $C_{12}H_{16}OOs$: C, 39.33; H, 4.40; Os, 51.90. Found: C, 39.48; H, 4.46; Os, 51.65. MS (70 eV), *m/z* 368 (62, M^+), 340 (71, $M^+ - CO$ or $M^+ - C_2H_4$), 338 (100, $M^+ - C_2H_6$), 312 (45, $M^+ - CO - C_2H_4$); IR (hexane) ν(CO) 1922 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.59 (s, $C_6\mathit{H}_3Me_3$), 1.94 (s, $C_6H_3\mathit{Me}_3$), 2.22 (m, [2H]) and 1.53 (m, [2H], C_2H_4).

Preparation of [(mes)Os(C_2D_4)(CO)] (7-*d*$_4$) occurred analogously as described for **7**, using **6**-*d*$_5$ (98 mg, 0.19 mmol) and NaH (ca. 150 mg) as starting materials, yield 58 mg (82%). Anal. Calcd for $C_{12}H_{12}D_4OOs$: C, 38.91, H + D, 5.43. Found: C, 38.92; H + D, 5.45. MS (70 eV), *m/z* 372 (54, M^+), 344 (5, $M^+ - CO$), 340 (100, $M^+ - C_2D_4$), 312 (42, $M^+ - CO - C_2D_4$); IR (hexane) ν(CO) 1921 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.58 (s, $C_6\mathit{H}_3Me_3$), 1.93 (s, $C_6H_3\mathit{Me}_3$).

Preparation of [(mes)OsCH_3(CO)H] (8). A solution of **4** (93 mg, 0.19 mmol) in 10 mL of THF/EtOH (100:1) was stirred after addition of an excess of Na/Hg for 30 min at room temperature. A color change from orange to pale yellow was observed. The solution was separated from the solid residue and was brought to dryness in vacuo. The crude product was dissolved in 2 mL of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade III). With benzene/hexane (1:1) a yellow fraction was eluted, from which after removing the solvent a yellow solid was obtained. It was purified by sublimation in vacuo (40 °C, 10^{-4} mbar), yield 55 mg (81%). Anal. Calcd for $C_{11}H_{16}OOs$: C, 37.28; H, 4.55. Found: C, 37.79; H, 4.46. MS (70 eV), *m/z* 356 (5, M^+), 340 (100, $M^+ - CH_4$), 312 (50, $M^+ - CH_4 - CO$); IR (hexane) ν(OsH) 2060, ν(CO) 1951 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.47 (s, $C_6\mathit{H}_3Me_3$), 1.87 (s, $C_6H_3\mathit{Me}_3$), 0.91 (s, $OsCH_3$), –10.16 (s, OsH).

Preparation of [(mes)OsH(CO)Cl] (9). A suspension of **3** (112 mg, 0.27 mmol) in 10 mL of methanol was treated at 0 °C with an excess of zinc powder (ca. 200 mg). The mixture was stirred at 0 °C for 60 min and then warmed to room temperature for 30 min. The solvent was removed in vacuo to give a red-brown residue which was extracted three times with 5 mL of benzene. The solution was filtered, and the filtrate was concentrated to ca. 1 mL. After slow addition of 10 mL of hexane, a bright yellow solid precipitated and was filtered off, washed with hexane, and dried in vacuo, yield 56 mg (55%). Anal. Calcd for $C_{10}H_{13}ClOOs$: C, 32.04; H, 3.49. Found: C, 31.61; H, 3.43. MS (70 eV), *m/z* 376 (1, M^+), 340 (2, $M^+ - HCl$); IR (KBr) ν(OsH) 2060, ν(CO) 1950 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.64 (s, $C_6\mathit{H}_3Me_3$), 2.02 (s, $C_6H_3\mathit{Me}_3$), –9.56 (s, OsH).

Preparation of [(mes)OsH_2(CO)] (10). A suspension of **3** (103 mg, 0.25 mmol) in 20 mL of liquid ammonia was treated at –78 °C with 2 mL of *tert*-butyl alcohol and an excess of sodium (ca. 300 mg). An immediate color change to deep blue was observed. After the cooling bath was removed, the mixture was stirred for 30 min, becoming yellow. The solvent was removed in vacuo, and the brown residue was extracted three times with 5 mL of benzene. The solution was filtered, the filtrate was brought to dryness, and the crude product was recrystallized from hexane at 25 to –78 °C to give a white microcrystalline powder, yield 38 mg (49%). Anal. Calcd for $C_{10}H_{14}OOs$: C, 35.28; H, 4.15; Os, 55.87. Found: C, 34.81; H, 4.10; Os, 55.60. MS (70 eV), *m/z* 342 (28, M^+), 340 (75, $M^+ - H_2$), 312 (36, $M^+ - H_2 - CO$); IR (C_6H_6) ν(OsH) 2060, ν(CO) 1935 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.83 (s, $C_6\mathit{H}_3Me_3$), 2.11 (s, $C_6H_3\mathit{Me}_3$), –11.03 (s, OsH_2).

Preparation of [(C_6H_6)OsH_2(CO)] (13) occurred analogously as described for **10**, using **11** (78 mg, 0.14 mmol) as starting material. After recrystallization from hexane a white microcrystalline solid was obtained, yield 20 mg (46%). Anal. Calcd for C_7H_8OOs: C, 28.18; H, 2.70. Found: C, 27.95; H, 2.63. MS (70 eV), *m/z* 300 (1, M^+), 298 (2, $M^+ - H_2$), 270 (2, $M^+ - H_2 - CO$); IR (C_6H_6) ν(OsH) 2060, ν(CO) 1945 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.85 (s, C_6H_6), –10.72 (s, OsH_2).

Preparation of [(C_6Me_6)RuH_2(CO)] (14) occurred analogously as described for **10**, using **12** (96 mg, 0.26 mmol) as starting material. The white microcrystalline product isolated after recrystallization from hexane still contained some C_6Me_6 as an impurity. **14** was therefore characterized by spectroscopic means: IR (C_6H_6) ν(RuH) 1965, ν(CO) 1925 cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.08 (s, C_6Me_6), –10.07 (s, RuH_2).

Preparation of [(mes)OsH_3(CO)]BF_4 (15). A solution of **10** (100 mg, 0.29 mmol) in 2 mL of dichloromethane was treated at –78 °C with ca. 10 drops of a solution of HBF_4 in ether. After addition of 10 mL of ether a white precipitate was obtained which was separated from the mother liquor, repeatedly washed with ether, and dried in vacuo, yield 74 mg (60%). Anal. Calcd for $C_{10}H_{15}BF_4OOs$: C, 28.05; H, 3.53. Found: C, 27.95; H, 3.32. IR (CH_2Cl_2) ν(CO) 2041 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 6.44 (s, $C_6\mathit{H}_3Me_3$), 2.73 (s, $C_6H_3\mathit{Me}_3$), –12.36 (s, br, OsH_3).

Preparation of [(mes)OsH(CO)$_2$]BF_4 (16). A stream of CO was passed for 75 min through a solution of **15** (50 mg, 0.12 mmol) in 7 mL of dichloromethane. After addition of 10 mL of ether a white precipitate was obtained which was separated from the mother liquor, repeatedly washed with ether, and dried in vacuo, yield 40 mg (73%). Anal. Calcd for $C_{11}H_{13}BF_4O_2Os$: C, 29.09; H, 2.88. Found: C, 29.06; H, 2.91. IR (CH_2Cl_2) ν(CO) 2067, 2019 cm^{-1}; ^{1}H NMR (acetone-*d*$_6$) δ 6.97 (s, $C_6\mathit{H}_3Me_3$), 2.88 (s, $C_6H_3\mathit{Me}_3$), –12.90 (s, OsH).

Preparation of [(mes)Os(CO)$_2$] (17). A suspension of **16** (100 mg, 0.22 mmol) in 6 mL of THF was treated with an excess of NaH (ca. 100 mg) and stirred for 30 min at room temperature. The solvent was removed in vacuo, and the residue extracted with 7 mL of benzene. The solution was filtered, the remaining solid was washed with 3 mL of benzene, and the combined filtrates were brought to dryness in vacuo. The residue was sublimed (40 °C, 10^{-4} mbar) to give a yellow microcrystalline powder, yield 39 mg (40%). Anal. Calcd for $C_{11}H_{12}O_2Os$: C, 36.06; H, 3.30; Os 51.91. Found: C, 35.65; H, 3.55; Os, 51.95. MS (70 eV), *m/z* 368

(57, M^+), 340 (46, $M^+ - CO$), 312 (42, $M^+ - 2CO$); IR (hexane) ν(CO) 1978, 1907 cm^{-1}; ^1H NMR (C_6D_6) δ 4.82 (s, $C_6H_3Me_3$), 1.90 (s, $C_6H_3Me_3$).

Preparation of [(mes)Os(C_2H_4)$_2$] (18). A suspension of 1 (105 mg, 0.14 mmol for $n = 2$) in 12 mL of ethanol was treated with an excess of dry Na_2CO_3 (ca. 100 mg). While a slow stream of ethylene was passed through the suspension, it was heated to 80 °C under continuous stirring. After 6 h the reaction mixture was cooled to room temperature, and the solvent was removed in vacuo. The residue was extracted three times with 20 mL of petroleum ether, the solution was filtered, and the filtrate was concentrated to ca. 1 mL in vacuo. After chromatography on Al_2O_3 (neutral, activity grade III) with benzene/hexane (1:5) a yellow fraction was obtained. It was brought to dryness and dried in vacuo to give a pale yellow microcrystalline solid, yield 48 mg (48%). Anal. Calcd for $C_{13}H_{20}Os$: C, 42.60; H, 5.50; Os, 51.90. Found: C, 42.49; H, 5.64; Os, 52.05. MS (70 eV), m/z 368 (24, M^+); ^1H NMR (C_6D_6) δ 4.58 (s, $C_6H_3Me_3$), 1.72 (s, $C_6H_3Me_3$), 2.04 (m, [4H], C_2H_4), 0.94 (m, [4H], C_2H_4).

Preparation of [(mes)Os(C_7H_8)] (19) occurred analogously as described for 18, starting from 1 (89 mg, 0.12 mmol for $n = 2$) and norbornadiene (0.91 g, 9.9 mmol). The reaction mixture was heated to 80 °C for 1 h and further worked up as described for 18 by using only hexane for chromatography. A pale yellow powder was obtained, yield 56 mg (58%). Anal. Calcd for $C_{16}H_{20}Os$: C, 47.74; H, 5.01. Found: C, 48.27; H, 5.28. MS (70 eV), m/z 404 (71, M^+); ^1H NMR (C_6D_6) δ 4.77 (s, $C_6H_3Me_3$), 1.91 (s, $C_6H_3Me_3$), 3.74 (m, CH), 2.64 (m, =CH—), 1.07 (t, $J_{HH} = 1.6$ Hz, CH_2).

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Registry No. 1, 126724-08-1; **2**, 126724-09-2; **3**, 126724-10-5; **4**, 123725-82-6; **5**, 126724-11-6; **5**-d_6, 126724-15-0; **6**, 126724-13-8; **6**-d_5, 126724-17-2; **7**, 123725-77-9; **7**-d_4, 123725-83-7; **8**, 123725-75-7; **9**, 126724-14-9; **10**, 123725-76-8; **11**, 109013-42-5; **12**, 71652-17-0; **13**, 126724-18-3; **14**, 126724-19-4; **15**, 126724-21-8; **16**, 126724-23-0; **17**, 123725-74-6; **18**, 126724-24-1; **19**, 126724-25-2; DMSO, 67-68-5; $OsCl_3$, 13444-93-4; [(mes)$OsCl_2$]$_2$, 94957-59-2; CO, 630-08-0; [CPh_3]PF_6, 437-17-2; 1,3,5-trimethylcyclohexa-1,4-diene, 4074-23-1; methylmagnesium iodide, 917-64-6; methyllithium, 917-54-4; ethylene, 74-85-1; norbornadiene, 121-46-0.

Dynamic Behavior and Rearrangements of Group 14 Organometallic Substituted Alkenylboranes

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Alkenylboranes 7 and 8 with a group 14 organometallic group ($R^2{}_3M$; M = Sn, Pb, R^2 = Me, Et, Ph) at the C=C double bond, in a cis position with respect to the boryl group, are obtained via organoboration of the corresponding alkynylstannanes (5) and -plumbanes (6) ($R^2{}_3M—C\equiv C—R^1$; R^1 = H, Me, ^{t}Bu, Ph) with trialkylboranes (R_3B, R = Et (**2a**), ^{i}Pr (**2b**)). Many of the lead compounds are thermally and photolytically unstable. The dialkylboryl group in 7 and 8 prefers the conformation 10, where the C_2B plane is perpendicular to the C=C—B plane as shown by dynamic ^1H and ^{13}C NMR spectra. In the alkene derivatives 7 and 8 cleavage of the =C—R bond occurs readily, re-forming the alkynylmetal compound (5, 6) and the trialkylboranes 2 (deorganoboration). Direct proof is given for this by two-dimensional $^1H/^1H$ exchange NMR spectra. The preferred structure 10 makes CB ($\sigma\pi$) interactions possible, weakening the =C—R bond, and together with a weak M—C= bond the organoboration becomes readily reversible. The structure 10 is also favorable for R^2/R exchange, which has been found to take place between lead and boron in 8, leading to alkenes 13 and 13′. Only one example for 8 has been found for cis/trans isomerization into 15. All products are characterized by their ^{11}B, ^{13}C, ^{119}Sn, and ^{207}Pb NMR data.

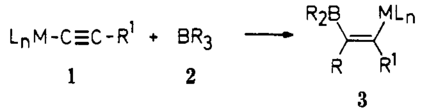
Introduction

Among the various reactive sites in alkynylmetal compounds (1)[1] the M—C≡C- fragment in particular offers great synthetic potential. Considering the polarity of that

$$L_nM-C\equiv C-R^1$$

1

fragment, an electrophile is likely to attack at either of the alkyne carbon atoms. The attack at the carbon atom adjacent to the metal may lead to cleavage of the M—C≡ bond, which is then followed by further reactions. We have found that triorganoboranes (**2**) react with various alkynylmetal compounds (M = Si,[2] Sn,[3] Pb,[4] Pt[5]) such that alkenes of type **3** are formed (eq 1). The metal fragment



(1)

$R^2{}_3M$ has migrated from one carbon atom to the other, and an organyl group (R) from boron together with the boryl group end up at the same carbon atom. In most cases these organoborations are quantitative and stereoselective (as shown). An intermediate (4) has been proposed[3] that

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