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Preparation of [(mes)Os(CNR)Cl$_2$] and Reactions of the Methyl Isocyanide Complex with Organolithium and Grignard Reagents. X-ray Crystal Structure of [(mes)Os(=C(NHCH$_3$)C$_6$H$_5$)(C$_6$H$_5$)$_2$]

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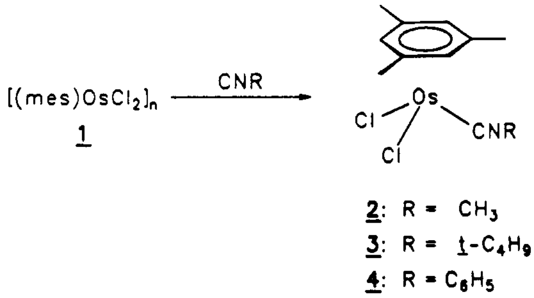
The isocyanide complexes [(mes)Os(CNR)Cl$_2$] (2-4) are prepared almost quantitatively from [(mes)OsCl$_2$]$_n$ (1) and CNR in dichloromethane. Reactions of 2 (R = CH$_3$) with CH$_3$Li and C$_6$H$_5$Li in hydrocarbon-ether give the dimethyl and diphenyl derivates [(mes)OsR$_2$(CNCH$_3$)] (5, 6) in excellent yields. Treatment of 2 with CH$_3$MgI leads to the formation of a mixture of [(mes)OsCH$_3$(CNCH$_3$)I] (7) and [(mes)Os(CNCH$_3$)I$_2$] (9), which can be separated by column chromatography. Analogously, from 2 and C$_6$H$_5$MgI, both [(mes)OsC$_6$H$_5$(CNCH$_3$)I] (8) and 9 have been obtained. In contrast, reaction of 2 with C$_6$H$_5$MgBr gives, besides [(mes)OsC$_6$H$_5$(CNCH$_3$)Br] (11), the carbene complex [(mes)Os(=C(NHCH$_3$)C$_6$H$_5$)(C$_6$H$_5$)$_2$] (10) as the main product. The X-ray crystal structure of 10 has been determined (monoclinic space group $P2_1/n$ with a = 12.402 (3) Å, b = 14.237 (2) Å, c = 13.622 (2) Å, β = 91.54 (1)°). The molecule possesses a piano-stool configuration with an Os-C(carbene) distance of 1.992 (5) Å.

Introduction

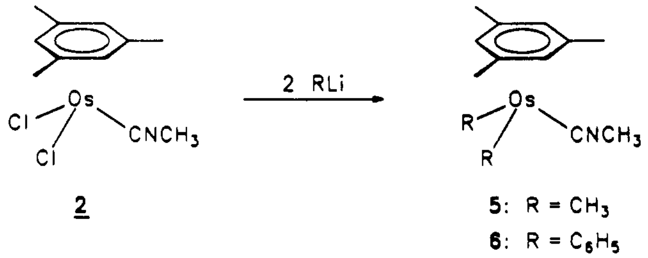
As an extension of earlier work from our laboratory on (arene)osmium(II) and osmium(0) complexes,[1,2] we have recently described a series of related compounds in which, besides the six-membered ring, one or two CO but no phosphane or phosphite ligands are coordinated to the metal.[3-5] We have found that in contrast to the half-sandwiches [(arene)Os(CO)(PR$_3$)] and [(arene)OsH$_2$(PR$_3$)], the corresponding dicarbonyl and carbonyl dihydrido metal derivatives, [(arene)Os(CO)$_2$] and [(arene)OsH$_2$(CO)], are photochemically more labile and thus useful starting materials for C-H activation studies both in matrix and in solution.[4,6] A surprising result was that the carbonyl hydrido methyl complex [(mes)OsH(CH$_3$)(CO)], which is the photoproduct from both [(mes)Os(CO)$_2$] and [(mes)OsH$_2$(CO)] in CH$_4$ matrices[4] and which can also be prepared from [(mes)OsCl$_2$]$_n$ or [(mes)Os(CO)Cl$_2$] on more conventional routes,[5,7] does not react with ligands such as CO or PMe$_3$ to give an acetyl(hydrido) metal derivative.

We therefore turned our attention to isocyanide osmium complexes in the hope that they offer a better chance for functionalization of the C-bound ligand. Previously, we have already reported the preparation of benzene osmium compounds [(C$_6$H$_6$)Os(CNR)(PMe$_3$)] which behave as metal bases and react with NH$_4$PF$_6$, CH$_3$I and ClAuPPh$_3$ to form salts of the corresponding cations [(C$_6$H$_6$)OsX(CNR)(PMe$_3$)]$^+$ (X = H, CH$_3$, AuPPh$_3$).[8] The reactions of the PF$_6$ salts of these cations with excess PMe$_3$ lead to displacement of the benzene ring and formation of the octahedral complexes *trans*-[OsX(CNR)(PMe$_3$)$_4$]PF$_6$.[8]

Scheme I



Scheme II



In the present paper we describe the synthesis of mesitylene(isocyanide)dichloroosmium(II) compounds and discuss the reactivity of one representative (with CNCH$_3$ as ligand) toward organolithium and Grignard reagents. The result of the X-ray structural analysis of the carbene complex [(mes)Os(=C(NHCH$_3$)C$_6$H$_5$)(C$_6$H$_5$)$_2$], which derives from [(mes)Os(CNCH$_3$)Cl$_2$] upon treatment with C$_6$H$_5$MgBr, is also reported.

Results

Preparation of the Dichloro Complexes [(mes)Os(CNR)Cl$_2$]. The bridging halide complex [(mes)OsCl$_2$]$_n$

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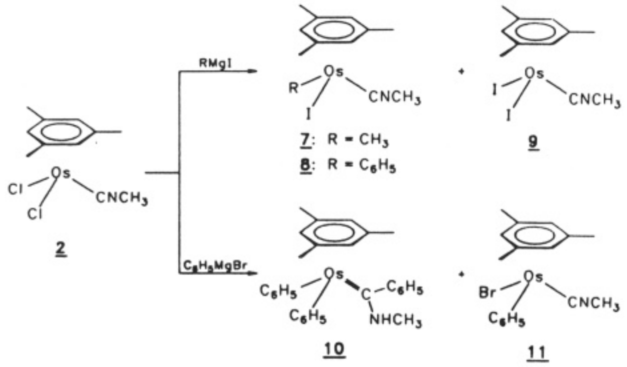
Scheme III



(1), which is either a polymer[5] or a dimer,[9] reacts with isocyanides CNR (R = CH_3, t-C_4H_9, C_6H_5) under similar conditions as with CO, CH_3CN, DMSO, and phosphines[5,10] to give the mononuclear compounds [(mes)Os(CNR)Cl_2] (**2–4**) (Scheme I). They are orange-yellow solids that are moderately air-stable and easily soluble in polar solvents such as CH_2Cl_2 or $CHCl_3$. The IR spectra of **2–4** show a strong CN stretching frequency at 2140–2180 cm^{-1}, which appears at about the same wavenumbers as that of the benzene osmium derivatives [(C_6H_6)Os(CNR)I_2] and [(C_6H_6)Os(CNR)(PMe_3)I]PF_6.[8]

Reactions of Compound 2 with Organolithium and Grignard Reagents. In two preceding papers on the chemistry of mesitylene osmium carbonyl and olefin complexes we have already described that the reactions of [(mes)Os(CO)Cl_2] with organolithium and Grignard reagents proceed differently.[5,11] This observation has also been made for **2** (which was chosen as a representative of the dichloro isocyanide compounds) as starting material. Treatment of a suspension of **2** with an ether solution of CH_3Li or with C_6H_5Li in cyclohexane/ether give the dimethyl- and diphenylosmium complexes **5** and **6** (Scheme II) in 78% and 89% yield. Both compounds are yellow air-sensitive solids, which have been characterized by elemental analysis and mass spectra. The thermal stability decreases in the order **2** > **6** > **5**, which is similar to that found for the carbonyl derivatives [(mes)Os(CO)X_2]. In the ^{1}H NMR spectrum of **5**, the signal of the osmium-bound CH_3 protons is found upfield (δ 0.88), indicative of the expected high electron density at the metal center.

The course of the reaction of **2** with RMgI (R = CH_3, C_6H_5) and C_6H_5MgBr depends on the type of Grignard reagent used. If a suspension of **2** in benzene is treated with an ether solution of CH_3MgI in the molar ratio of 1:1.5, two products, [(mes)OsCH_3($CNCH_3$)I] (**7**) and [(mes)Os($CNCH_3$)I_2] (**9**) (Scheme III), are obtained, which can be separated by chromatographic techniques. In contrast to the behavior of [(mes)Os(CO)Cl_2] toward CH_3MgI, even with an excess of the Grignard reagent the formation of the dimethylosmium complex **5** cannot be observed. Compound **9** has also been prepared by metathesis from **2** and KI in almost quantitative yield.

Most interestingly, the reactions of **2** with phenylmagnesium halides give different mixture of products, depending on the type of Grignard reagent used. Whereas with C_6H_5MgI (molar ratio 1:1), in analogy to the reaction of **2** with CH_3MgI, a mixture of [(mes)OsC_6H_5($CNCH_3$)I] (**8**) and **9** is formed, the major component upon treatment of **2** with C_6H_5MgBr followed by chromatography on Al_2O_3 is the carbene osmium complex [(mes)Os(=C($NHCH_3$)C_6H_5)(C_6H_5)$_2$] (**10**). In addition, also the bromo phenyl compound [(mes)OsC_6H_5($CNCH_3$)Br] (**11**) (Scheme III) has been isolated. Although a 3.4-fold excess of the Grignard reagent has been used, the formation of the diphenyl metal derivative **6** cannot be detected.

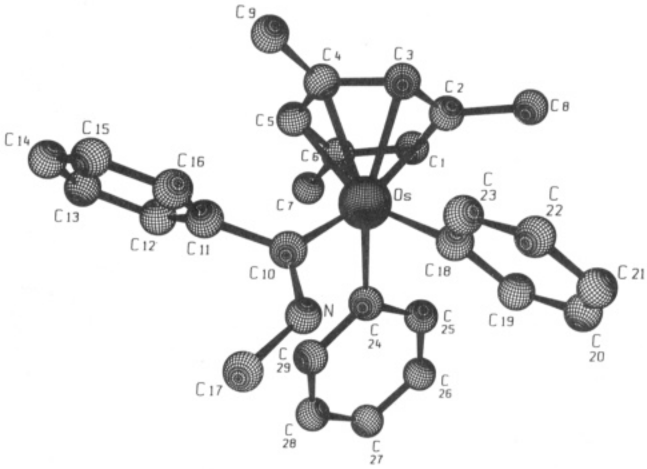


Figure 1. SCHAKAL[19] drawing of complex **10**.

Table I. Selected Bond Distances and Angles with Esd's of 10

Bond Distances, Å					
Os–C1	2.300 (5)	Os–C5	2.280 (5)	Os–C24	2.092 (5)
Os–C2	2.321 (5)	Os–C6	2.247 (5)	N–C10	1.326 (6)
Os–C3	2.239 (5)	Os–C10	1.992 (5)	N–C17	1.473 (6)
Os–C4	2.271 (5)	Os–C18	2.100 (4)	C10–C11	1.503 (7)

Bond Angles, deg			
C10–Os–C18	87.0 (2)	C11–C10–Os	123.8 (4)
C10–Os–C24	87.3 (2)	C11–C10–N	113.4 (4)
C18–Os–C24	90.1 (2)	Os–C10–N	122.8 (4)
C10–N–C17	128.0 (4)		

Torsional Angles,[a] deg			
CENT–Os–C10–N	−164.3 (5)	C18–Os–C10–C11	150.6 (6)
CENT–Os–C10–C11	16.4 (7)	C24–Os–C10–N	60.2 (6)
C18–Os–C10–N	−30.1 (7)	C24–Os–C10–C11	−119.2 (6)

[a] CENT = centroid of the mesitylene ring.

The carbene complex **10** is an orange air-sensitive solid that is quite volatile and decomposes at ca. 100 °C. The most characteristic feature in the ^{1}H NMR spectrum is the doublet at δ 1.66 for the NHCH_3 protons, the splitting originating from coupling with the NH nucleus. In the ^{13}C NMR, a signal at 221.9 appears, which is assigned to the carbene carbon atom. We note that for the complex [Os(=$CHCH_3$)(CO)(PPh_3)$_2Cl_2$], which has been recently described by Roper et al.,[12] the $CHCH_3$ signal is found at δ 227, whereas in the cationic carbene osmium derivatives [(C_6H_6)Os(=$\overline{CCH_2CH_2CHR'O}$)($PR_3$)I]$^+$, which are somewhat related in structure to **10**, the carbene carbon resonance appears at δ 260–285.[13]

Molecular Structure of 10. A single-crystal X-ray diffraction investigation of compound **10** confirms the structural proposal shown in Scheme III. The SCHAKAL drawing (Figure 1) reveals that the osmium is coordinated by the mesitylene ring, the two phenyl groups, and the aminocarbene ligand, the phenyl substituent of which is directed away from the metal-bound C_6H_5 units. The bond angles C10–Os–C18, C10–Os–C24, and C18–Os–C24 (see Table I) are near to 90°, which is in agreement with the

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piano-stool arrangement of the molecule.

The Os═C bond length [1.992 (5) Å] is similar to that in $[Os({=}CHPh)(CO)(PPh_3)_2Cl_2]$ [1.94 (1) Å],[12] $[Os({=}CF_2)(NO)(PPh_3)_2Cl]$ [1.967 (4) Å],[12] and $[(C_6H_6)Os({=}CCH_2CH_2CH_2O)(PMe\text{-}t\text{-}Bu_2)I]^+$ [1.953 (2) Å][13] and almost identical with that in $[Os_3(CO)_9({=}C(OCH_3)CH_3)(\mu\text{-}H)(\mu\text{-}COCH_3)]$ [1.99 (2) Å].[14] The C10–N distance [1.326 (6) Å] is significantly shorter than the distance C17-N [1.473 (6) Å], indicating a substantial double-bond character of the carbon–nitrogen bond. In agreement with the proposed sp^2 hybridization of the carbene carbon atom, the groups attached to C10 are exactly coplanar. The dihedral angle between the best planes through the atoms Os, C10, N, C11 and the mesitylene ring is 100.4 (2)°. Other torsional angles are given in Table I.

Although the mesitylene ring is exactly planar, the Os–C1 to Os–C6 distances differ by ca. 0.08 Å. The greater bond lengths (Os–C1 and Os–C2) are found opposite to C10, an observation reflecting the strong trans influence of the carbene ligand.

Concluding Remarks

The work presented in this paper has shown that interaction of the new isocyanide complexes $[(mes)Os(CNR)Cl_2]$ with methylating and phenylating reagents can lead to the formation of either OsR_2 or Os(R)X species. Whereas from **2** ($R = CH_3$) and LiR ($R = CH_3$, C_6H_5) the dimethyl- and diphenylosmium compounds **5** and **6** are obtained, treatment of the same starting material with CH_3MgI or C_6H_5MgX (X = Br, I) gives in each case at least two products. Besides the iodo methyl and phenyl and the bromo phenyl osmium derivatives (**7**, **8**, **11**), from **2** and C_6H_5MgBr a carbene complex **10** is formed, which probably originates from nucleophilic attack of the Grignard reagent at the isocyanide carbon atom followed by protonation on the nitrogen. As far as Fischer-type carbene complexes are concerned, both Darensbourg[15] and Casey[16] have previously observed that not only organolithium but also Grignard reagents can be used to transform a CO into an oxycarbene ligand. We are not aware that an analogous generation of an aminocarbene ligand from a coordinated isocyanide and RMgX has been reported.

The possibility that the solvent benzene takes part in the formation of the $C(NHCH_3)C_6H_5$ ligand can be excluded. If the reaction of **2** with C_6H_5MgBr is performed in C_6D_6–ether, no deuterium is incorporated into the product. If on the other hand the aluminum oxide used for the chromatographic workup of the reaction mixture is deactivated with D_2O, instead of **10** the monodeuterated complex $[(mes)Os({=}C(NDCH_3)C_6H_5)(C_6H_5)_2]$ (**10**-d_1) has been isolated. The IR spectrum of **10**-d_1 shows a characteristic ND stretching frequency at 2485 cm^{-1}, compared with the NH absorption of **10** at 3345 cm^{-1}.

We finally note that two carbene rhodium compounds of composition $[(C_5Me_5)Rh({=}C(NHR)R')X_2]$ (**12a**, X = Cl; **12b**, X = Br), which are related in structure to **10**, have recently been described in the literature.[17,18] Following their work on intermolecular oxidative addition of C–H bonds to metal centers, Jones and co-workers prepared the (isocyanide)*p*-tolylrhodium derivatives $[(C_5Me_5)Rh(p\text{-}C_6H_4CH_3)(CNR)X]$ ($R = CH_2C(CH_3)_3$; X = Cl, Br), which after addition of NH_4X react to give the dichloro and dibromo carbene rhodium complexes **12a**,**b** in 90% yield. The aminocarbene ligand is thought to be formed by insertion of the isocyanide into the rhodium–tolyl bond and subsequent protonation of the iminoacyl nitrogen atom with NH_4^+. A similar phenyl migration has not been observed with **6**, **8**, or **11** in the presence of nucleophiles, from which we conclude that the generation of the carbene ligand in **10** occurs by external attack of the Grignard reagent at the coordinated isocyanide. We are currently exploring the possibility of preparing other arene carbene osmium complexes from various isocyanide metal precursors and also of using the recently described carbonylosmium compounds $[(arene)OsR_2(CO)]$[11] as starting materials.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting material $[(mes)OsCl_2]_n$ (**1**) was prepared as described recently.[5] NMR spectra were recorded on a JEOL FX 90 Q and a Bruker AC 200 instruments, IR spectra on a Perkin-Elmer 1420 infrared spectrometer, and mass spectra on a Varian MAT CH 7 instrument.

Preparation of Complexes $[(mes)Os(CNR)Cl_2]$ (2–4). A suspension of **1** (900 mg, 1.18 mmol for $n = 2$) in 40 mL of dichloromethane was treated with the isocyanide ($R = CH_3$, 259 mg, 6.30 mmol; $R = t\text{-}C_4H_9$, 480 mg, 5.75 mmol; $R = C_6H_5$, 605 mg, 5.87 mmol) and stirred for 3 h at 40 °C ($R = CH_3$) or for 2.5 h ($R = t\text{-}C_4H_9$ and C_6H_5) at room temperature. The solution was filtered and the residue repeatedly washed with CH_2Cl_2 (ca. 30 mL). The filtrate was concentrated to ca. 5–10 mL in vacuo, and ether (ca. 20 mL) was added. An orange-yellow precipitate was obtained, which was filtered off, washed with ether and hexane, and dried in vacuo, yielding 800 mg (80%) of **2**, 1.02 g (93%) of **3**, and 1.11 g (97%) of **4**; mp of **3** 166 °C dec and of **4** 214 °C dec.

2: Anal. Calcd for $C_{11}H_{15}Cl_2NOs$: C, 31.28; H, 3.54; N, 3.32. Found: C, 31.18; H, 3.66; N, 3.45 IR (KBr) ν(CN) 2187 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 5.26 (s, $C_6\mathit{H}_3Me_3$), 3.78 (s, $CNCH_3$), 2.31 (s, $C_6H_3\mathit{Me}_3$).

3: Anal. Calcd for $C_{14}H_{21}Cl_2NOs$: C, 36.20; H, 4.56; N, 3.02. Found: C, 36.46; H, 4.61; N, 3.01. MS (70 eV), *m/z* 465 (2, M^+), 382 (15, $M^+ - CNC_4H_9$); IR (KBr) ν(CN) 2162 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 5.23 (s, $C_6\mathit{H}_3Me_3$), 2.30 (s, $C_6H_3\mathit{Me}_3$), 1.54 (s, $t\text{-}C_4H_9$).

4: Anal. Calcd for $C_{16}H_{17}Cl_2NOs$: C, 39.67; H, 3.54; N, 2.89. Found: C, 39.88; H, 3.83; N, 3.01. MS (70 eV), *m/z* 485 (0.3, M^+), 120 (34, $C_6H_3Me_3^+$); IR (KBr) ν(CN) 2142 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.39 (m, C_6H_5), 5.34 (s, $C_6\mathit{H}_3Me_3$), 2.39 (s, $C_6H_3\mathit{Me}_3$).

Preparation of $[(mes)Os(CH_3)_2(CNCH_3)]$ (5). A suspension of **2** (200 mg, 0.47 mmol) in 10 mL of benzene was treated at 5 °C with 0.75 mL of a 1.25 M solution of CH_3Li in ether (0.94 mmol). After stirring for 2.5 h, a small amount of Al_2O_3 (ca. 100 mg) was added and the solvent was removed in vacuo. The residue was dissolved in 3 mL of benzene and the solution chromatographed on Al_2O_3 (basic, activity grade III). With hexane a yellow fraction was eluted from which after removing the solvent a yellow microcrystalline solid was isolated, yield 139 mg (78%), mp 76 °C dec. Anal. Calcd for $C_{13}H_{21}NOs$: C, 40.92; H, 5.55; N, 3.67. Found: C, 41.02; H, 5.46; N, 3.73. MS (70 eV), *m/z* 383 (14, M^+), 368 (13, $M^+ - CH_3$), 312 (1, $(mes)Os^+$); IR (CH_2Cl_2) ν(CN) 2102 cm^{-1}; ^1H NMR (C_6D_6, 90 MHz) δ 4.38 (s, $C_6\mathit{H}_3Me_3$), 2.68 (s, $CNCH_3$), 1.96 (s, $C_6H_3\mathit{Me}_3$), 0.88 (s, $OsCH_3$).

Preparation of $[(mes)Os(C_6H_5)_2(CNCH_3)]$ (6). A suspension of **2** (100 mg, 0.24 mmol) in 5 mL of benzene was treated at 5 °C with 0.24 mL of a 2.0 M solution of C_6H_5Li in cyclohexane/ether. After stirring for 30 min, the reaction mixture was worked up as described for **5**. With hexane an orange fraction was eluted, which contained a small amount of **10** (9 mg, 6%). With dichloromethane, a yellow fraction was eluted from which after removing the solvent a yellow microcrystalline solid was isolated, yield 108 mg (89%); mp 129 °C dec. Anal. Calcd for $C_{23}H_{25}NOs$: C, 54.63;

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H, 4.98; N, 2.77. Found: C, 54.49; H, 4.93; N, 2.67. MS (70 eV), *m/z* 507 (36, M^+), 466 (2, $M^+ - CNCH_3$), 430 (2, $M^+ - C_6H_5$), 389 (3, $(mes)OsC_6H_5^+$), 353 (100, $M^+ - 2C_6H_5$); IR (CH_2Cl_2) ν(CN) 2123 cm^{-1}; ^1H NMR (C_6D_6, 90 MHz) δ 7.87 (m, 4 H, C_6H_5), 7.19 (m, 6 H, C_6H_5), 4.41 (s, $C_6\mathit{H}_3Me_3$), 2.47 (s, $CNCH_3$), 1.65 (s, $C_6H_3\mathit{Me}_3$).

Preparation of [(mes)OsCH$_3$(CNCH$_3$)I] (7) and [(mes)Os(CNCH$_3$)I$_2$] (9). A suspension of **2** (150 mg, 0.36 mmol) in 5 mL of benzene was treated at 5 °C with 2.2 mL of a 0.25 M solution of CH_3MgI in ether (0.55 mmol). After warming to room temperature, the reaction mixture was stirred for 15 min, and then a small amount of Al_2O_3 (ca. 100 mg) was added (to destroy the excess of CH_3MgI). The solvent was removed in vacuo and after the residue was dissolved in 3 mL of C_6H_6/CH_2Cl_2 (1:1), the solution was chromatographed on Al_2O_3 (basic, activity grade III). With benzene, an orange fraction and, subsequently, with dichloromethane a red fraction were eluted. Both fractions were brought to dryness in vacuo to give an orange-yellow microcrystalline solid of **7** (yield 41 mg, 23%) and a red microcrystalline solid of **9** (yield 163 mg, 75%), mp of **7** 148 °C dec.

7: Anal. Calcd for $C_{12}H_{18}INOs$: C, 29.21; H, 3.68; N, 2.84. Found: C, 29.30; H, 3.61; N, 2.63. MS (70 eV), *m/z* 495 (7, M^+), 480 (13, $M^+ - CH_3$), 439 (15, $(mes)OsI^+$); IR (CH_2Cl_2) ν(CN) 2140 cm^{-1}; ^1H NMR (C_6D_6, 90 MHz) δ 4.42 (s, $C_6\mathit{H}_3Me_3$), 2.59 (s, $CNCH_3$), 2.00 (s, $C_6H_3\mathit{Me}_3$), 1.73 (s, $OsCH_3$).

9: Anal. Calcd for $C_{11}H_{15}I_2NOs$: C, 21.83; H, 2.50; N, 2.31. Found: C, 22.43; H, 2.72; N, 2.48. IR (KBr) ν(CN) 2173 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 5.36 (s, $C_6\mathit{H}_3Me_3$), 3.92 (s, $CNCH_3$), 2.56 (s, $C_6H_3\mathit{Me}_3$).

A second procedure for the preparation of **9** is as follows: A solution of **2** (100 mg, 0.24 mmol) in 15 mL of acetone was treated with an excess of KI (ca. 300 mg). After it was stirred for 3 h at 60 °C, the solution was cooled and then the solvent was removed in vacuo. The residue was extracted twice with 6 mL of CH_2Cl_2 each, and the combined extracts were concentrated to ca. 3 mL. After addition of hexane, a dark red precipitate was obtained, which was filtered off, repeatedly washed with hexane, and dried in vacuo, yield 129 mg (90%).

Preparation of [(mes)OsC$_6$H$_5$(CNCH$_3$)I] (8). A suspension of **2** (105 mg, 0.25 mmol) in 10 mL of benzene was treated at 5 °C with an equimolar amount of C_6H_5MgI in ether. After warming to room temperature and stirring for 30 min, some Al_2O_3 was added. The solvent was removed in vacuo, the residue was dissolved in 2 mL of benzene, and the solution was chromatographed on Al_2O_3 (basic, activity grade III). With hexane, an orange fraction was eluted, which contained a small quantity (13 mg, 9%) of **10**. With C_6H_6/CH_2Cl_2 (5:1) a yellow fraction was eluted from which after removing the solvent a yellow microcrystalline solid **8** (41 mg, 30%) was obtained. Finally, a red fraction was eluted from which **9** (88 mg, 58%) was isolated; mp of **8** 176 °C dec. Anal. Calcd for $C_{26}H_{31}INOs$: C, 36.76; H, 3.63; N, 2.52. Found: C, 36.76; H, 3.68; N, 2.72. MS (70 eV), *m/z* 557 (17, M^+), 516 (0.3, $M^+ - CNCH_3$), 480 (5, $M^+ - C_6H_5$), 439 (9, $(mes)OsI^+$), 430 (20, $M^+ - I$), 389 (14, $(mes)OsC_6H_5^+$), 353 (1, $(mes)OsCNCH_3^+$); IR (CH_2Cl_2) ν(CN) 2160 cm^{-1}; ^1H NMR (C_6D_6, 90 MHz) δ 7.91 (m, 2 H, C_6H_5), 7.14 (m, 3 H, C_6H_5), 4.42 (s, $C_6\mathit{H}_3Me_3$), 2.45 (s, $CNCH_3$), 1.82 (s, $C_6H_3\mathit{Me}_3$).

Preparation of [(mes)Os(=C(NHCH$_3$)C$_6$H$_5$)(C$_6$H$_5$)$_2$] (10) and [(mes)OsC$_6$H$_5$(CNCH$_3$)Br] (11). A suspension of **2** (105 mg, 0.25 mmol) in 10 mL of benzene was treated with 3.6 mL of a 0.25 M solution of C_6H_5MgBr in ether (0.9 mmol). After stirring for 30 min, a small amount of Al_2O_3 (ca. 100 mg) was added and the solvent was removed in vacuo. The residue was dissolved in 2 mL of benzene and the solution was chromatographed on Al_2O_3 (basic, activity grade III). With benzene/hexane (1:1) an orange fraction was eluted, which was brought to dryness in vacuo. Recrystallization of the residue from hexane gave orange crystals of **10**, yield 68 mg (71%), mp 99 °C dec. With dichloromethane, a second orange fraction was eluted from which after removing the solvent an orange microcrystalline powder of **11** was obtained, yield 29 mg (23%), mp 188 °C dec.

Table II. Crystallographic Data for 10

formula	$C_{29}H_{31}NOs$
formula wt	583.77
cryst size, mm	0.15 × 0.4 × 0.5
cryst syst	monoclinic
space group	$P2_1/n$
cell dimens determn	23 reflecns, 12° < θ < 15°
a, Å	12.402 (3)
b, Å	14.237 (2)
c, Å	13.622 (2)
β, deg	91.54 (1)
V, Å^3	2404.3
Z	4
d_{calcd}, g cm^{-3}	1.61
diffractometer	Enraf-Nonius CAD 4
radiatn (graphite monochromated)	Mo Kα (0.709 30 Å)
temp, °C	20 ± 1
μ, cm^{-1}	53.2
scan method	$\omega/2\theta$
2θ (max), deg	46
total no. of rflns scanned	3682
no. of unique rflns	3320
no. of obsd rflns ($F_o > 3\sigma(F_o)$)	2618
no. of params refined	280
R	0.028
R_w	0.031
rfln/param ratio	9.35
residual electron density, e Å^{-3}	+0.67/−0.42

Table III. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	β, Å^2
Os	0.23643 (2)	0.19085 (2)	0.00061 (2)	3.110 (5)
N	0.2175 (5)	0.2397 (5)	0.2084 (5)	4.2 (2)
C1	0.2561 (7)	0.1859 (7)	−0.1667 (6)	4.9 (2)
C2	0.1666 (7)	0.1322 (6)	−0.1466 (6)	4.4 (2)
C3	0.1766 (7)	0.0604 (6)	−0.0744 (6)	4.4 (2)
C4	0.2796 (7)	0.0390 (6)	−0.0305 (6)	4.4 (2)
C5	0.3685 (7)	0.0944 (6)	−0.0547 (6)	4.4 (2)
C6	0.3576 (7)	0.1712 (7)	−0.1176 (6)	4.5 (2)
C7	0.4532 (7)	0.2304 (7)	−0.1402 (7)	5.9 (2)
C8	0.0569 (8)	0.1487 (8)	−0.1967 (8)	6.9 (3)
C9	0.2905 (8)	−0.0466 (6)	0.0350 (6)	5.3 (2)
C10	0.2684 (6)	0.1864 (6)	0.1445 (5)	3.6 (2)
C11	0.3525 (6)	0.1238 (6)	0.1915 (5)	3.6 (2)
C12	0.4605 (6)	0.1311 (6)	0.1693 (6)	4.2 (2)
C13	0.5359 (7)	0.0714 (7)	0.2137 (7)	5.6 (2)
C14	0.5025 (8)	0.0057 (8)	0.2800 (7)	6.4 (2)
C15	0.3958 (9)	−0.0028 (7)	0.3020 (7)	6.1 (3)
C16	0.3206 (7)	0.0557 (6)	0.2585 (6)	4.7 (2)
C17	0.2455 (7)	0.2553 (7)	0.3128 (6)	5.6 (2)
C18	0.0779 (5)	0.2275 (6)	0.0357 (6)	3.4 (2)
C19	0.0231 (6)	0.3104 (7)	0.0027 (6)	4.3 (2)
C20	−0.0835 (6)	0.3247 (7)	0.0220 (6)	5.3 (2)
C21	−0.1416 (6)	0.2640 (7)	0.0758 (6)	5.0 (2)
C22	−0.0923 (6)	0.1842 (7)	0.1107 (6)	4.9 (2)
C23	0.0155 (6)	0.1671 (6)	0.0919 (6)	4.4 (2)
C24	0.2811 (6)	0.3324 (5)	0.0054 (6)	3.8 (2)
C25	0.2512 (7)	0.3939 (6)	−0.0745 (7)	4.8 (2)
C26	0.2861 (7)	0.4868 (7)	−0.0784 (8)	5.8 (2)
C27	0.3531 (7)	0.5241 (7)	−0.0073 (8)	6.1 (3)
C28	0.3840 (7)	0.4674 (7)	0.0718 (8)	5.7 (2)
C29	0.3494 (6)	0.3754 (7)	0.0775 (7)	4.9 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = {}^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

10: Anal. Calcd for $C_{29}H_{31}NOs$: C, 59.67; H, 5.35; N, 2.40. Found: C, 59.62; H, 5.55; N, 2.46. MS (70 eV), *m/z* 585 (3, M^+), 507 (18, $M^+ - C_6H_6$), 353 (11, $(mes)Os(CNCH_3)^+$); IR (CH_2Cl_2) ν(NH) 3345 cm^{-1}; ^1H NMR (C_6D_6, 200 MHz) δ 7.82–6.84 (m, C_6H_5), 4.47 (s, $C_6\mathit{H}_3Me_3$), 1.66 (d, J(HH) = 5.3 Hz, NCH_3), 1.38 (s, $C_6H_3\mathit{Me}_3$), signal of the NH proton not observed; ^{13}C NMR (C_6D_6, 50.3 MHz) δ 221.9 (s, Os=C), 155.0, 152.7, 143.9, 129.0, 127.4, 127.2, 126.8, 123.3, 121.2 (all s, C_6H_5), 99.9 (s, *C*Me of $C_6H_3Me_3$), 89.0 (s, *C*H of $C_6H_3Me_3$), 36.3 (s, NCH_3), 17.6 (s, $C\mathit{C}H_3$ of $C_6H_3Me_3$).

11: Anal. Calcd for $C_{17}H_{20}BrNOs$: C, 40.16; H, 3.96; N, 2.75. Found: C, 40.53; H, 4.27; N, 2.87. MS (70 eV), *m/z* 509 (0.3, M^+), 120 (33, $C_6H_3Me_3^+$); IR (CH_2Cl_2) ν(CN) 2167 cm^{-1}; ^1H NMR (C_6D_6, 90 MHz) δ 7.86 (m, 2 H of C_6H_5), 7.18 (m, 3 H of C_6H_5), 4.47 (s, $C_6\mathit{H}_3Me_3$), 2.50 (s, $CNCH_3$), 1.88 (s, $C_6H_3\mathit{Me}_3$).

X-ray Structural Analysis of 10. Single crystals were grown from hexane at −15 °C. Crystal data collection parameters are summarized in Table II. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied; the minimal transmission was 81%. The structure was solved by direct methods (SHELXS-86). Atomic coordinates (see Table III) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares. The positions of all hydrogen atoms were calculated according to ideal geometry and were refined by the riding method. For other details see Table II.

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Supplementary Material Available: Drawing of complex 10 showing the atom numbering scheme and tables of bond distances, bond angles, least-squares planes, positional parameters, and general displacement parameter expressions (11 pages); tables of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Cluster Chemistry. 69.[1] Unusual Transformation of Triarylphosphine Ligands on a Pentanuclear Ruthenium Cluster. X-ray Structures of Two Phases of $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$

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The reaction between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ and PPh_3 gave a monosubstituted complex, which in refluxing CH_2Cl_2 was transformed into $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$ (4, Ar = Ph). This complex contains a distorted-octahedral PRu_5 cluster with the PPh_2 groups bridging basal Ru–Ru edges, together with a C_2Ph_2 ligand spanning an Ru_3 face. A similar reaction with $P(tol)_3$ (tol = $C_6H_4Me\text{-}p$) gave $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ar)(\mu\text{-}PPh_2)(\mu\text{-}PAr_2)(CO)_{10}$ (4, Ar = tol). The net reaction occurring on the Ru_5 cluster is between PAr_3 (Ar = Ph, tol) and C_2PPh_2 to form PPh, PAr_2, and PhC_2Ar ligands. The molecular structure of 4 (Ar = Ph) was determined from X-ray studies on solvent-free and solvated modifications. $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$: triclinic, space group $P\bar{1}$, $a = 17.282$ (4) Å, $b = 13.558$ (2) Å, $c = 13.498$ (4) Å, $\alpha = 61.94$ (1)°, $\beta = 81.06$ (2)°, $\gamma = 85.03$ (2)°, $Z = 2$, $R = 0.037$, $R' = 0.036$ for 6084 observed reflections. $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}\cdot CH_2Cl_2$: triclinic, space group $P\bar{1}$, $a = 21.399$ (10) Å, $b = 12.658$ (15) Å, $c = 12.447$ (8) Å, $\alpha = 59.00$ (7)°, $\beta = 79.20$ (4)°, $\gamma = 74.22$ (8)°, $Z = 2$, $R = 0.067$, $R' = 0.085$ for 5442 observed reflections.

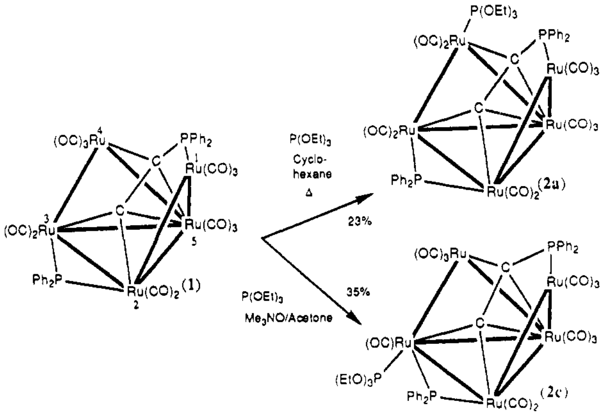
Introduction

We have recently shown that the preferred sites of CO substitution by tertiary phosphines or phosphites in $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1; Scheme I) are at Ru(3) (thermally induced reactions) or at Ru(4) (in Me_3NO-facilitated reactions) to give isomers of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PR_3)$ (**2a**, **2c**).[1] In studies with $P(OEt)_3$, no subsequent modification of the group 15 ligand occurred; the product obtained with PMe_2Ph was noted as being unstable, but the decomposition products were not characterised. We have now found that facile rearrangement reactions of triarylphosphines occur with 1; these are described below.

Results and Discussion

Two methods of substituting CO ligands in 1 by PPh_3 were examined. The first method, using Me_3NO to remove a CO ligand, permitted the isolation of dark brown crystalline $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)$ (3, Ar = Ph). In the FAB mass spectrum, a molecular ion was found at

Scheme I. Reactions of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1) with $P(OEt)_3$



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