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Syntheses and Reactions of (Halomethylidyne)trihydridotriruthenium and -osmium Nonacarbonyl Clusters

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Halomethylidyne clusters $H_3M_3(\mu_3\text{-CX})(CO)_9$ (M = Ru, X = Cl, Br; M = Os, X = Br) are prepared by treatment of $H_3M_3(\mu_3\text{-COCH}_3)(CO)_9$ with the corresponding boron trihalide. The ruthenium cluster $H_3Ru_3(\mu_3\text{-CBr})(CO)_9$ reacts with $AlCl_3$ and then methanol to give $H_3Ru_3(\mu_3\text{-CCO}_2CH_3)(CO)_9$ and with $AlCl_3$ in C_6H_5R (R = H, CH_3) to give $H_3Ru_3(\mu_3\text{-CC}_6H_5R)(CO)_9$. Under basic conditions the cluster forms $H_3Ru_3(\mu_3\text{-COC}_2H_5)(CO)_9$ with ethanol and $HRu_3(\mu\text{-CN}(C_2H_5)_2)(CO)_{10}$ with diethylamine. With tri-*n*-butyltin hydride, $H_3Ru_3(\mu_3\text{-CH})(CO)_9$ is prepared from the bromide derivative.

Introduction

Since their discovery over 20 years ago, methylidynetricobalt complexes of the general formula $Co_3(\mu_3\text{-CY})(CO)_9$ (Y = halogen, alkyl, aryl, carboxyl, etc.) have become perhaps the most extensively studied metal clusters. As a result, much is known about the structures, physical and chemical properties, and bonding of these unusual molecules.[1] While the $Co_3(\mu_3\text{-CY})(CO)_9$ clusters exhibit exceptional thermal and air stability, only a handful of related clusters of metals other than cobalt are known. Until recently, examples from the iron triad were limited to $H_3Ru_3(\mu_3\text{-CCH}_3)(CO)_9$,[2] $H_3Os_3(\mu_3\text{-CCH}_3)(CO)_9$,[3] and $H_3Os_3(\mu_3\text{-CH})(CO)_9$.[4] Thus, until now it has not been possible to extend the wealth of knowledge about the properties of methylidynetricobalt clusters to other M_3CY systems.

Recently one of us reported convenient and high-yield syntheses of the methylidyne clusters $H_3Ru_3(\mu_3\text{-COCH}_3)(CO)_9$ and $H_3Os_3(\mu_3\text{-COCH}_3)(CO)_9$.[5] These molecules are isostructural (see Figure 1) with the $Co_3(\mu_3\text{-CY})(CO)_9$ series and represent the first functionalized alkylidyne clusters of the iron triad. Because of their ease of preparation, we felt that these clusters might provide convenient entries into the series of clusters $H_3M_3(\mu_3\text{-CY})(CO)_9$ (M = Ru or Os) analogous to that of the cobalt system. Furthermore, these molecules would offer additional possibilities for chemical reactivity and structural studies by virtue of the three hydride ligands. For these reasons we have explored the chemistry of the $H_3M_3(\mu_3\text{-CY})(CO)_9$ system. We now report the syntheses of $H_3Ru_3(\mu_3\text{-CY})(CO)_9$, Y = Cl, Br, CO_2CH_3, C_6H_5, $C_6H_5CH_3$, OC_2H_5, and H, and of $H_3Os_3(\mu_3\text{-CBr})(CO)_9$ and compare these clusters with their cobalt analogues.

Experimental Section

Methods of Characterization. Infrared spectra (Table I) were recorded on cyclohexane solutions with a Beckman 4250 spectrophotometer and were calibrated by using the 2138.5-cm^{-1} absorption for cyclohexane or using polystyrene. Proton NMR spectra were obtained on Varian CFT-80 or EM-360 instruments. Mass spectra were recorded by Mr. Carter Cook of the University of Illinois Mass Spectroscopy Laboratory, using a Varian CH-5 instrument at 70 eV and a solids probe temperature of 25–150 °C. Elemental analyses were performed by Galbraith Laboratories.

Chemicals. The clusters $H_3Ru_3(\mu_3\text{-COCH}_3)(CO)_9$ and $H_3Os_3(\mu_3\text{-COCH}_3)(CO)_9$ were synthesized as previously described.[5a] Boron tribromide and boron trichloride were obtained from Aldrich and aluminum trichloride was obtained from MCB, and all were used without further purification. Tributyltin hydride was purchased from Alfa.

Table I. Infrared Spectra

compd	IR (in cyclohexane), 2150–1600 cm^{-1}
$H_3Ru_3(\mu_3\text{-COCH}_3)(CO)_9$	2106 w, 2076 s, 2036 s, 2029 m, sh, 2014 m, 2000 w
$H_3Os_3(\mu_3\text{-COCH}_3)(CO)_9$	2107 w, 2077 s, 2074 s, 2022 vs, 2013 m, 2008 m, 1995 w
$H_3Ru_3(\mu_3\text{-CBr})(CO)_9$	2086 s, 2080 w, 2040 s, 2030 m, 2000 vw, 1992 vw
$H_3Os_3(\mu_3\text{-CBr})(CO)_9$	2087 s, 2069 vw, 2032 vs, 2021 m, 1990 w
$H_3Ru_3(\mu_3\text{-CCl})(CO)_9$	2087 s, 2080 w, 2042 s, 2029 m, 1990 w
$H_3Ru_3(\mu_3\text{-CCO}_2CH_3)(CO)_9$	2114 vw, 2090 s, 2081 m, 2040 s, 2030 m, 2021 w, 1685 w
$H_3Ru_3(\mu_3\text{-CC}_6H_5)(CO)_9$	2106 vw, 2080 s, 2035 s, 2031 m, sh, 2020 m, 2017 m, sh, 1993 vw
$H_3Ru_3(\mu_3\text{-CC}_6H_4CH_3)(CO)_9$	2108 vw, 2075 s, 2036 s, 2020 m
$H_3Ru_3(\mu_3\text{-COC}_2H_5)(CO)_9$	2107 w, 2077 vs, 2036 vs, 2029 m, 2014 m, 2000 w
$HRu_3(\mu\text{-CN}(C_2H_5)_2)(CO)_{10}$	2096 w, 2056 s, 2046 s, 2022 s, 2008 s, 1999 m, 1996 s, 1985 w
$H_3Ru_3(\mu_3\text{-CH})(CO)_9$	2081 s, 2034 s, 2019 m, 1985 w

$H_3Ru_3(\mu_3\text{-CBr})(CO)_9$. To a stirred solution of $H_3Ru_3(\mu_3\text{-COCH}_3)(CO)_9$ (125 mg, 0.208 mmol) in dichloromethane (100 mL) was added boron tribromide (50 μL, 0.538 mmol) under nitrogen. After 30 min the solution was evaporated to dryness, and methanol (10 mL) was added to destroy any residual boron tribromide. Then the product mixture was purified by preparative thin-layer chromatography on silica gel eluting with dichloromethane–hexane (1:5 by volume). A single bright yellow band yielded $H_3Ru_3(\mu_3\text{-CBr})(CO)_9$ (116 mg, 86%) after extraction.

^{1}H NMR ($CDCl_3$): τ 27.80 (s). *m/e* 660 ($^{104}Ru_3{}^{81}Br$). Anal. Calcd for $Ru_3C_{10}H_3O_9Br$: C, 18.46; H, 0.46; Br, 12.31. Found: C, 18.56; H, 0.43; Br, 11.97.

$H_3Os_3(\mu_3\text{-CBr})(CO)_9$. To a solution of $H_3Os_3(\mu_3\text{-COCH}_3)(CO)_9$ (86 mg, 0.10 mmol) in dichloromethane (20 mL) was added boron tribromide (40 μL, 0.4 mmol) under nitrogen with stirring. After 5 min the solution was evaporated to dryness with vacuum and methanol (5 mL) was added. Then the solution was evaporated to dryness and the residue was purified by thin-layer chromatography on silica gel eluting with dichloromethane–hexane (1:5). The only observed product was $H_3Os_3(\mu_3\text{-CBr})(CO)_9$ (89 mg, 98%).

^{1}H NMR ($CDCl_3$): τ 29.2 (s). *m/e* 924 ($^{192}Os_3{}^{81}Br$). Anal. Calcd for $Os_3C_{10}H_3O_9Br$: C, 13.08; H, 0.33. Found: C, 13.24; H, 0.30.

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(1) (a) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97. (b) Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* **1973**, *6*, 73.

(2) (a) Canty, A. J.; Johnson, B. F. G.; Lewis, J.; Norton, J. R. *J. Chem. Soc., Chem. Commun.* **1972**, 1331. (b) Sheldrick, G. M.; Yesinowski, J. P. *J. Chem. Soc., Dalton Trans.* **1975**, 873.

(3) (a) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Chem. Commun.* **1973**, 277. (b) Yesinowski, J. P.; Bailey, D. *J. Organomet. Chem.* **1974**, *65*, C27.

(4) (a) Azam, K. A.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 472. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

(5) (a) Keister, J. B. *J. Chem. Soc., Chem. Commun.* **1979**, 214. (b) Johnson, B. F. G.; Lewis, J.; Orpen, A. G.; Raithby, P. R.; Suss, G. *J. Organomet. Chem.* **1979**, *173*, 187. (c) Gavens, P. D.; Mays, M. J. *Ibid.* **1978**, *162*, 389.

0020-1669/80/1319-2304$01.00/0

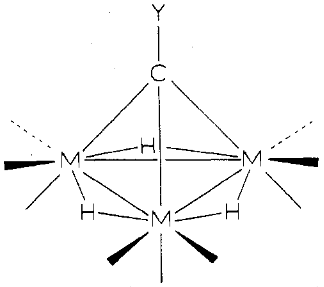

Figure 1. Structure of $H_3M_3(\mu_3\text{-}CY)(CO)_9$ (M = Ru, Y = OCH_3, OC_2H_5, Cl, Br, CO_2CH_3, C_6H_5, $C_6H_4CH_3$, H; M = Os, Y = OCH_3, Br).

$H_3Ru_3(\mu_3\text{-}CCl)(CO)_9$. To a solution of $H_3Ru_3(\mu_3\text{-}COCH_3)(CO)_9$ (147 mg, 0.244 mmol) in dichloromethane (70 mL) was added boron trichloride (1.0 mL, 1.0 mmol) under nitrogen. After 2 h the solution was evaporated to dryness with vacuum and the residue was purified by preparative thin-layer chromatography on silica gel eluting with dichloromethane–hexanes (1:10). The product $H_3Ru_3(\mu_3\text{-}CCl)(CO)_9$ was isolated after extraction (66 mg, 45%).

^1H NMR (CD_2Cl_2): τ 27.87 (s). m/e 616 ($^{104}Ru_3{}^{37}Cl$). Anal. Calcd for $Ru_3C_{10}H_3O_9Cl$: C, 19.82; H, 0.50; Cl, 5.86; Ru, 50.04. Found: C, 19.70; H, 0.38; Cl, 5.60; Ru, 49.80.

$H_3Ru_3(\mu_3\text{-}CCO_2CH_3)(CO)_9$. To a solution of $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ (90 mg, 0.138 mmol) in dry dichloromethane (50 mL) was added aluminum trichloride (122 mg, 0.91 mmol) with carbon monoxide bubbling through the solution. After 10 min TLC showed no starting material remaining and methanol (1 mL) was added. The resulting solution was treated with 10% hydrochloric acid, and the organic layer was dried over magnesium sulfate, filtered, and evaporated to dryness. The residue was purified by preparative thin-layer chromatography on silica gel eluting with dichloromethane–hexanes (1:5). The second yellow band was extracted with dichloromethane–methanol to give $H_3Ru_3(\mu_3\text{-}CCO_2CH_3)(CO)_9$ (33 mg, 38%).

^1H NMR ($CDCl_3$): τ 27.82 (s, 3 H), 5.96 (s, 3 H). m/e 638 ($^{104}Ru_3$). Anal. Calcd for $Ru_3C_{12}H_6O_{11}$: C, 22.88; H, 0.96; Ru, 48.18. Found: C, 23.01; H, 1.00; Ru, 47.99.

$H_3Ru_3(\mu_3\text{-}CC_6H_5)(CO)_9$. In a 50-mL, three-necked flask equipped with nitrogen inlet, stirring bar, and dropping funnel was placed benzene (5 mL) and aluminum trichloride (200 mg, 1.5 mmol). Then a solution of $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ (84 mg, 0.13 mmol) in benzene (10 mL) and dichloromethane (10 mL) was added dropwise. The solution turned red after addition. After 15 min the red solution was poured into 50 mL of dilute hydrochloric acid (10%) and the organic layer separated. The aqueous portion was washed twice with 10-mL portions of dichloromethane. Then the organic portions were combined, dried over magnesium sulfate, filtered, and evaporated to dryness. The residue was purified by preparative thin-layer chromatography on silica gel eluting with cyclohexane to give one yellow band, which was extracted with dichloromethane to give upon evaporation yellow crystalline $H_3Ru_3(\mu_3\text{-}CC_6H_5)(CO)_9$ (80 mg, 95%).

^1H NMR ($CDCl_3$): τ 2.3–2.9 (m, 5 H), 27.49 (s, 3 H). m/e 656 ($^{104}Ru_3$). Anal. Calcd for $Ru_3C_{16}H_8O_9$: C, 29.66; H, 1.25. Found: C, 29.68; H, 1.33.

$H_3Ru_3(\mu_3\text{-}CC_6H_4CH_3)(CO)_9$. To a mixture of aluminum trichloride (325 mg, 2.43 mmol) in toluene (25 mL) in a three-necked, 100-mL flask equipped with nitrogen inlet and stirring bar was added a solution of $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ (200 mg, 0.31 mmol) in toluene (25 mL) from a dropping funnel. After 15 min the red mixture was filtered and the filtrate was evaporated to dryness and purified by preparative thin-layer chromatography on silica gel eluting with dichloromethane–hexanes (1:5 v/v) to yield $H_3Ru_3(\mu_3\text{-}CC_6H_4CH_3)(CO)_9$ (54 mg, 26%). The red solid in the filter was treated with methanol and similarly purified to give additional product (75 mg, 37%).

^1H NMR (acetone-d_6): τ 27.35 (s, 3 H), 7.70 (s, 1.7 H), 7.67 (s, 1.3 H), 2.3–3.1 (m, 4 H). m/e 670 ($^{104}Ru_3$). Anal. Calcd for $Ru_3C_{17}H_{10}O_9$: C, 30.85; H, 1.52. Found: C, 31.03; H, 1.57.

$H_3Ru_3(\mu_3\text{-}COC_2H_5)(CO)_9$. To a solution of $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ (196 mg, 0.302 mmol) in distilled ethanol (45 mL) under nitrogen was added sodium ethoxide (56 mg, 0.83 mmol). After the mixture was stirred for 5 min at 35 °C, ammonium chloride was added and the solution was evaporated to dryness with vacuum. Then the residue was purified by preparative thin-layer chromatography on silica gel eluting with dichloromethane-hexanes (1:10 v/v). The first band eluted was unreacted $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ (20 mg, 10%). The second band was $H_3Ru_3(\mu_3\text{-}COC_2H_5)(CO)_9$ (134 mg, 72%).

^1H NMR ($CDCl_3$): τ 27.20 (s, 3 H), 8.30 (t, 3 H), 5.92 (q, 2 H), J = 6.9 Hz. m/e 644 ($^{104}Ru_3$). Anal. Calcd for $Ru_3C_{12}H_8O_{10}$: C, 23.41; H, 1.30; Ru, 49.27. Found: C, 23.33; H, 1.23; Ru, 49.52.

$HRu_3(\mu\text{-}CN(C_2H_5)_2)(CO)_{10}$. To a solution of $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ (220 mg, 0.34 mmol) in hexane (50 mL) under 1 atm of carbon monoxide was added diethylamine (0.35 mL, 3.4 mmol). The solution was heated for 3.5 h at 55 °C with stirring. Then the solution was evaporated to dryness and the residue was purified by chromatography on silica gel eluting with dichloromethane–hexanes (1:10 v/v). The first band eluted was unreacted $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ (61 mg, 28%). The second band was $HRu_3(\mu\text{-}CN(C_2H_5)_2)(CO)_{10}$ (65 mg, 28%). The product is also formed in the absence of carbon monoxide.

^1H NMR ($CDCl_3$): τ 24.60 (s, 1 H), 8.38 (t, 6 H), 5.70 (q, 4 H), J = 7.4 Hz. m/e 677 ($^{104}Ru_3$). Anal. Calcd for $Ru_3C_{15}H_{11}O_{10}N$: C, 26.95; H, 1.65; N, 2.10. Found: C, 26.26; H, 1.89; N, 2.09.

$H_3Ru_3(\mu_3\text{-}CH)(CO)_9$. To a solution of $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ (121 mg, 0.187 mmol) in dry hexanes (25 mL) under nitrogen was added tributyltin hydride (0.15 mL, 0.56 mmol). The solution was stirred at 50 °C with carbon monoxide bubbling through for 3.5 h. Then the solution was evaporated to dryness with vacuum, and the residue was purified by thin-layer chromatography on silica gel eluting with hexane. The second yellow band was $H_3Ru_3(\mu_3\text{-}CH)(CO)_9$ (18 mg, 17%).

^1H NMR ($CDCl_3$): τ 27.82 (s, 3 H), 0.25 (s, 1 H). m/e 580 ($^{104}Ru_3$). Anal. Calcd for $Ru_3C_{10}H_4O_9$: C, 21.01; H, 0.71. Found: C, 21.14; H, 0.79.

Results

Syntheses and Characterizations of $H_3M_3(\mu_3\text{-}CX)(CO)_9$ (M = Ru, X = Cl, Br; M = Os, X = Br). One of the most extensively studied members of the alkylidynetricobalt series is $Co_3(\mu_3\text{-}CCl)(CO)_9$, and its chemistry is well developed. To get the best comparison of the chemistry of the $H_3M_3(\mu_3\text{-}CY)(CO)_9$ systems with that of the cobalt analogue, it was desirable to prepare halogen derivatives from $H_3M_3(\mu_3\text{-}COCH_3)(CO)_9$. This was readily accomplished in high yield by treating the methoxy compounds with an excess of the appropriate boron trihalide in dichloromethane:

$$H_3Ru_3(\mu_3\text{-}COCH_3)(CO)_9 + BX_3\ (X = Cl, Br) \xrightarrow{25\ ^\circ C} H_3Ru_3(\mu_3\text{-}CX)(CO)_9$$

$$H_3Os_3(\mu_3\text{-}COCH_3)(CO)_9 + BBr_3 \xrightarrow{25\ ^\circ C} H_3Os_3(\mu_3\text{-}CBr)(CO)_9$$

The halide products are easily purified by thin-layer chromatography after destruction of unreacted boron trihalide. The ruthenium clusters are bright yellow crystalline solids, while $H_3Os_3(\mu_3\text{-}CBr)(CO)_9$ is pale yellow. All are air-stable; in particular, $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ is considerably more stable to oxidation than the methoxy precursor and is a convenient starting material for functionalization of the methylidyne carbon.

The compounds $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (X = Cl, Br) and $H_3Os_3(\mu_3\text{-}CBr)(CO)_9$ have been fully characterized by infrared, ^1H NMR, and mass spectroscopy, as well as by elemental analysis. The infrared spectra (Table I) in the terminal carbonyl region are very similar to those of the methoxy precursors, but the absorptions are shifted to slightly higher frequencies, consistent with the electron-withdrawing nature of the halide substituent. Each compound displays a single high-field resonance in the ^1H NMR spectrum attributable to three equivalent bridging hydride ligands. The mass spectrum for each displays the molecular ion and ions derived from successive loss of carbonyl ligands down to the bare M_3CX^+ fragment and finally the M_3C^+ ion. Although the three hydride ligands are observed in the highest mass envelope, they are gradually lost during fragmentation and because of the number of isotopes for each composition the average number of hydrogens in each ion is difficult to determine.

Doubly charged ions $H_mM_3CX(CO)_{9-n}^{2+}$, $n = 0$–9, are quite intense for $H_3Os_3(\mu_3\text{-}CBr)(CO)_9$ but very weak for the ruthenium clusters.

With the halide derivatives in hand the reaction chemistry of these molecules was compared with that of $Co_3(\mu_3\text{-}CCl)(CO)_9$. Our work has focused upon three types of reactions: substitution of the halogen, promoted by aluminum trihalides, nucleophilic displacements, and free radical substitution. Our work has concerned almost exclusively reactions of the ruthenium derivatives, but the osmium clusters are expected to behave similarly.[6]

Halide Substitutions Promoted by Aluminum Trichloride. Treatment of $Co_3(\mu_3\text{-}CCl)(CO)_9$ with aluminum trichloride in inert solvents results in the formation of a moderately stable "acylium" cation $Co_3(CCO)(CO)_9^+$. This species has been isolated as the hexafluorophosphate salt, but its structure is still unknown. Upon the addition of nucleophiles, such as alcohols or primary or secondary amines, the cation rapidly reacts to give carboxylic acid derivatives $Co_3(\mu_3\text{-}CY)(CO)_9$, $Y = CO_2R$, $C(O)NR_2$, etc.[1a,7]

The reaction of $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ with aluminum trichloride is similar to that observed for the cobalt analogue. Treatment of a dichloromethane solution of the ruthenium cluster under either a nitrogen or carbon monoxide atmosphere with excess aluminum trichloride causes gradual darkening of the yellow solution, presumably due to the formation of the $H_3Ru_3(CCO)(CO)_9$ cation. Upon the addition of methanol the color of the solution immediately darkens to orange, and after chromatography $H_3Ru_3(\mu_3\text{-}CCO_2CH_3)(CO)_9$ is isolated in 38% yield.

Characterization of $H_3Ru_3(\mu_3\text{-}CCO_2CH_3)(CO)_9$ by infrared, ^1H NMR, and mass spectroscopy is consistent with the proposed structure (Figure 1). The infrared spectrum (Table I) between 2150 and 1900 cm^{-1} is very similar to those of the other methylidynetriruthenium clusters; the C=O stretch of the ester moiety appears at 1685 cm^{-1}.[8] The ^1H NMR spectrum displays two singlets of equal intensity at τ 5.96 and 27.82, assigned to the methyl group and hydrides, respectively. The molecular ion and the usual fragmentation pattern are observed in the mass spectrum.

Another reaction of $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ promoted by aluminum trichloride in the presence of arenes gives arylmethylidyne clusters. Treatment of a benzene solution of the bromide derivative with excess aluminum trichloride produces $H_3Ru_3(\mu_3\text{-}CC_6H_5)(CO)_9$ in 90% yield. Similarly, the same reaction with toluene gives $H_3Ru_3(\mu_3\text{-}CC_6H_4CH_3)(CO)_9$ in 63% yield as an inseparable mixture of approximately equal amounts of two isomers, presumed to be ortho and para. Characterization of these two compounds by infrared, ^1H NMR, and mass spectroscopy (see Experimental Section) gives results very similar to other $H_3Ru_3(\mu_3\text{-}CY)(CO)_9$ clusters. These reactions are very similar to the reported Friedel–Crafts reactions with $Co_3(\mu_3\text{-}CX)(CO)_9$ (X = Cl, Br).[9]

Halide Substitutions by Nucleophiles under Basic Conditions. Carboxylic acid derivatives of the methylidynetricobalt cluster are also produced from $Co_3(\mu_3\text{-}CX)(CO)_9$ (X = Cl, Br) with nucleophiles under basic conditions. Thus, $Co_3(\mu_3\text{-}CCO_2CH_3)(CO)_9$ is formed with triethylamine in methanol and $Co_3(\mu_3\text{-}CC(O)N(C_2H_5)_2)(CO)_9$ from diethylamine after 3.5 h in benzene.[10] The mechanisms of these reactions are not well understood. Direct nucleophilic substitution is considered unlikely and carbonylated products are not always formed. For example, $Co_3(\mu_3\text{-}CSC_6H_5)(CO)_9$ is formed from $Co_3(\mu_3\text{-}CCl)(CO)_9$ and benzethiol in the presence of trimethylamine.[11]

In contrast to the cobalt analogues, base-catalyzed nucleophilic attack on $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ does not give carbonylated products. Treatment of an ethanolic solution with excess sodium ethoxide yields exclusively $H_3Ru_3(\mu_3\text{-}COC_2H_5)(CO)_9$. Even under a carbon monoxide atmosphere the ester derivative is not formed; instead the ether product eliminates dihydrogen and is carbonylated to yield $HRu_3(\mu\text{-}COC_2H_5)(CO)_{10}$. The infrared, ^1H NMR, and mass spectra of these two species are fully comparable to those for the methyl analogues previously characterized.[5]

Diethylamine also reacts differently with $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ than with the cobalt analogue. In either the presence or absence of carbon monoxide a slow reaction occurs at 50 °C to give exclusively $HRu_3(\mu\text{-}CN(C_2H_5)_2)(CO)_{10}$. This compound is analogous to previously reported $HRu_3(\mu\text{-}CN(CH_3)_2)(CO)_{10}$, for which the crystal structure has been determined,[12] and has been fully characterized. The presumed intermediate in this reaction, $H_3Ru_3(\mu_3\text{-}CN(C_2H_5)_2)(CO)_9$, must be less stable than the final product because of the extra stabilization associated with the $\mu\text{-}C^-{=}NR_2^+$ resonance form. This stabilization is, of course, more important with nitrogen than with oxygen, and it has proved impossible to hydrogenate $HRu_3(\mu\text{-}CN(C_2H_5)_2)(CO)_{10}$ to $H_3Ru_3(\mu_3\text{-}CN(C_2H_5)_2)(CO)_9$.

Reduction with Tributyltin Hydride. The prototype methylidyne cluster is $Co_3(\mu_3\text{-}CH)(CO)_9$ and the methylidyne analogues for ruthenium and osmium are important because of the special spectroscopic and chemical characteristics of the C–H bond. The osmium analogue $H_3Os_3(\mu_3\text{-}CH)(CO)_9$ has been previously synthesized by Shapley and Calvert[4b] in a two-step procedure from $H_2Os_3(CO)_{10}$ and diazomethane, but this method cannot be used for the ruthenium cluster. We have prepared $H_3Ru_3(\mu_3\text{-}CH)(CO)_9$ by reduction of $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ with tri-*n*-butyltin hydride.

When a solution of the bromide derivative is heated at 50 °C in the presence of excess tri-*n*-butyin hydride, a slow reaction occurs over several hours, and after chromatography, $H_3Ru_3(\mu_3\text{-}CH)(CO)_9$ is isolated in 17% yield. The infrared spectrum of the simplest methylidynetriruthenium cluster is very similar to those of other members of the series (see Table I). As for $H_3Os_3(\mu_3\text{-}CH)(CO)_9$ the methinyl proton resonance occurs at very low field (τ 0.25), while the chemical shift of the three equivalent hydride ligands is similar to those of the other $H_3Ru_3(\mu_3\text{-}CY)(CO)_9$ clusters.[13] The mass spectrum displays the molecular ion and ions derived from successive loss of carbonyls down to the bare Ru_3C fragment.

Reactions of $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ with Carbon Nucleophiles. Aryl Grignard reagents have been reported to give arylmethylidyne clusters in moderate yields from $Co_3(\mu_3\text{-}CX)(CO)_9$ (X = Cl, Br).[14] The mechanism for this reaction is not known, but it has been suggested that nucleophilic attack at a carbonyl ligand, forming an unstable metal acyl, is involved. However, no direct substitution is observed with alkyl Grignards; rather, all products are acid or ester derivatives formed upon destruction of the excess Grignard with water or alcohols.

For $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ three sites are available for attack by carbon nucleophiles—the methylidyne carbon, the carbonyl ligands, and the metal hydrides. In our hands no aryl derivatives have been isolated from reactions of this cluster with

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(6) Shapley, J. R., personal communication.

(7) Seyferth, D.; Williams, G. H.; Nivert, C. L. *Inorg. Chem.* **1977**, *16*, 758.

(8) The value for the ester C=O stretch for $Co_3(\mu_3\text{-}CCO_2CH_3)(CO)_9$ is 1695 cm^{-1}.

(9) Dolby, R.; Robinson, B. H. *J. Chem. Soc., Dalton Trans.* **1972**, 2046.

(10) Seyferth, D.; Nivert, C. L. *J. Organomet. Chem.* **1976**, *113*, C65.

(11) Seyferth, D.; Rudie, C. N.; Merola, J. S. *J. Organomet. Chem.* **1978**, *144*, C26.

(12) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843.

(13) The chemical shift of the methinyl proton of $Co_3(CH)(CO)_9$ is τ −2.1 (Seyferth, D.; Hallgren, J. E.; Hung, P. L. K. *J. Organometal. Chem.* **1973**, *50*, 265).

(14) Dolby, R.; Robinson, B. H. *J. Chem. Soc., Dalton Trans.* **1973**, 1794.

LiC_6H_5, C_6H_5MgBr, or $CH_3C_6H_4MgBr$ under conditions similar to those used for the cobalt clusters. Alkyl Grignards also gave no alkyl derivatives. Instead, in each case extensive decomposition occurred and the only compounds isolated were the starting material and the ether derivative $H_3Ru_3(\mu_3\text{-}COCH_3)(CO)_9$ resulting from reaction of $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ with methanol during the workup.

Discussion

The physical and chemical properties of the $H_3M_3(\mu_3\text{-}CY)(CO)_9$ series (M = Ru, Y = OCH_3, OC_2H_5, Cl, Br, CO_2CH_3, C_6H_5, $C_6H_4CH_3$, H; M = Os, Y = OCH_3, OC_2H_5, Br) appear, as expected, to be similar in many respects to those of the well-known $Co_3(\mu_3\text{-}CY)(CO)_9$ series. The methylidynetriruthenium clusters are, however, significantly less stable to oxygen or heat than the osmium or cobalt analogues. Additionally, the ruthenium and osmium clusters can undergo reactions involving loss of dihydrogen not available to the cobalt clusters. While this work has concerned almost exclusively ruthenium clusters, the osmium analogues are expected to behave similarly.

The most significant difference between the methylidyne clusters of ruthenium and of cobalt observed in this work is revealed by the reactions of the halide derivatives with nucleophiles under basic reaction conditions. Both $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ and $Co_3(\mu_3\text{-}CBr)(CO)_9$ form "acylium" cations upon treatment with aluminum trichloride and carboxylic acid derivatives upon subsequent treatment with nucleophiles. However, while the cobalt cluster also forms such products from nucleophiles under basic conditions, e.g., $Co_3(\mu_3\text{-}CCO_2CH_3)(CO)_9$ from methanol/triethylamine, $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$ gives only ether products. This difference may be due to the greater propensity of cobalt for carbonylation reactions, but clearly the reasons for it are not understood and stabilities of the respective intermediate cations may be important.

The hydride ligands of $H_3Ru_3(\mu_3\text{-}COR)(CO)_9$ (R = CH_3, C_2H_5) enable the cluster to undergo reactions not available to the cobalt analogue. At 100 °C under a carbon monoxide atmosphere $H_3Ru(\mu_3\text{-}COCH_3)(CO)_9$ slowly loses dihydrogen and reverts to $HRu_3(\mu\text{-}COCH_3)(CO)_{10}$. The μ-$COCH_3$ group is favorable because of the stabilization afforded by the $C^-{=}OCH_3^+$ resonance form.[5] This resonance form is more important for the amino derivatives because of the lower electronegativity of nitrogen and, thus, $H_3Ru_3(\mu_3\text{-}CNR_2)(CO)_9$ cannot be formed either by hydrogenation of $HRu_3(\mu\text{-}CNR_2)(CO)_{10}$ or by attack of NHR_2 on $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$.

The methylidyne clusters $H_3M_3(\mu_3\text{-}CY)(CO)_9$ may be expected to display an even richer chemistry than the cobalt series. These clusters offer possibilities for novel reactions involving loss of dihydrogen and coordination of donor ligands, as well as for coupling reactions involving the methylidyne fragment. Further work in this area is in progress.

Registry No. $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$, 73746-95-9; $H_3Os_3(\mu_3\text{-}CBr)(CO)_9$, 73746-96-0; $H_3Ru_3(\mu_3\text{-}CCl)(CO)_9$, 73746-97-1; $H_3Ru_3(\mu_3\text{-}CCO_2CH_3)(CO)_9$, 73746-98-2; $H_3Ru_3(\mu_3\text{-}CC_6H_5)(CO)_9$, 73746-99-3; $H_3Ru_3(\mu_3\text{-}CC_6H_4\text{-}o\text{-}CH_3)(CO)_9$, 73747-00-9; $H_3Ru_3(\mu_3\text{-}CC_6H_4\text{-}p\text{-}CH_3)(CO)_9$, 73747-01-0; $H_3Ru_3(\mu_3\text{-}COC_2H_5)(CO)_9$, 73747-02-1; $HRu_3(\mu\text{-}CN(C_2H_5)_2)(CO)_{10}$, 73747-03-2; $H_3Ru_3(\mu_3\text{-}CH)(CO)_9$, 63280-43-3; $H_3Ru_3(\mu_3\text{-}COCH_3)(CO)_9$, 71562-47-5; $H_3Os_3(\mu_3\text{-}COCH_3)(CO)_9$, 73747-04-3; BBr_3, 10294-33-4; BCl_3, 10294-34-5; methanol, 67-56-1; benzene, 71-43-2; toluene, 108-88-3; ethanol, 64-17-5; diethylamine, 109-89-7.

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Coordination Geometry of the Tridentate Chelating Ligand 2,2′-Bis(*o*-diphenylphosphino)-*trans*-stilbene (bdpps). Crystal Structures of the Complexes (bdpps)ClRh^I·CH_2Cl_2, (bdpps)ClRh^{III}, and (bdpps)Cl_3Ir^{III}

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The crystal and molecular structures of the complexes (bdpps)ClRh^I·CH_2Cl_2, **1**, (bdpps)Cl_3Rh^{III}, **2**, and (bdpps)Cl_3Ir^{III}, **3**, (bdpps = o-$Ph_2PC_6H_4CH{=}CHC_6H_4PPh_2$-$o$), have been determined by three-dimensional X-ray structural analysis using data collected by counter methods. Compound **1** crystallizes in space group $P\bar{1}$ with a = 9.3781 (6) Å, b = 20.7484 (10) Å, c = 9.3768 (6) Å, α = 93.12 (1)°, β = 76.80 (1)°, γ = 101.26 (1)°, and Z = 2. Crystals of **2** and **3** are isomorphous, of space group $C2/c$, with Z = 4 and a = 17.3288 (9) Å, b = 10.6979 (6) Å, c = 17.9021 (9) Å, and β = 99.89 (1)° for **2** and a = 17.3352 (10) Å, b = 10.7097 (6) Å, c = 17.9308 (9) Å, and β = 99.86 (1)° for **3**. The structures have been solved by conventional heavy-atom techniques and were refined by least-squares methods to final conventional R factors of 0.036 (**1**, 4428 independent reflections), 0.020 (**2**, 2391 reflections), and 0.033 (**3**, 2698 reflections). Important bond lengths are Rh(I)–Cl = 2.344 (2) Å, Rh(III)–Cl = 2.344 (1) Å, Ir(III)–Cl = 2.359 (1) Å, Rh(I)–P = 2.285 (2) Å, Rh(III)–P = 2.385 (1) Å, Ir(III)–P = 2.383 (1) Å, Rh(I)–C(olefin) = 2.101 (5) Å, Rh(III)–C(olefin) = 2.238 (2) Å, and Ir(III)–C(olefin) = 2.203 (3) Å. In the M(III) derivatives (**2** and **3**), the coordinated olefin is approximately parallel to the P–M–P axis, while in the Rh(I) derivative (**1**), the olefin is approximately perpendicular to this axis. The differences in orientation are shown to arise from a combination of electronic preferences with the simple geometric requirements of the chelating ligand.

Introduction

It has been shown[2] that diphenyl-*o*-tolylphosphine undergoes a coupling and dehydrogenation reaction on heating with $RhCl_3\cdot 3H_2O$, in high-boiling alcohols, to give the complex (bdpps)ClRh^I, **1** (bdpps = o-$Ph_2PC_6H_4$-t-$CH{=}CHC_6H_4PPh_2$-o, **4**), in low yield. Compound **1** is more efficiently prepared by reacting 2,2′-bis(diphenylphosphino)dibenzyl with $RhCl_3\cdot 3H_2O$.[3,4] Subsequent treatment with

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(2) Bennett, M. A.; Longstaff, P. A. *J. Am. Chem. Soc.* **1969**, *91*, 6266.

(3) Bennett, M. A.; Clark, P. W.; Robertson, G. B.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1972**, 1011.

0020-1669/80/1319-2307$01.00/0