Journal of Organometallic Chemistry, 219 (1981) C9—C12
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESES OF THE NEW TRINUCLEAR IONS $[Ru_3(CO)_{11}]^{2-}$ AND $[Os_3(CO)_{11}]^{2-}$

COLLEEN C. NAGEL, JEFFERY C. BRICKER, DONNA G. ALWAY and SHELDON G. SHORE*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

(Received June 24th, 1981)

Summary

Stoichiometric reduction of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ with K and Ca, respectively; yields the two new cluster dianions $[Os_3(CO)_{11}]^{2-}$ and $[Ru_3(CO)_{11}$ which have been isolated and characterized. Temperature-dependent ^{13}C NMR spectra for $[Os_3(CO)_{11}]^{2-}$ and infrared spectra of $[Os_3(CO)_{11}]^{2-}$ and $[Ru_3(CO)_{11}]^{2-}$ suggest a similar structure for these dianions in which there is a single edge-bridging carbonyl.

The trinuclear anions of the iron triad $[HFe_3(CO)_{11}]^-$, $[HRu_3(CO)_{11}]^-$, and $[HOs_3(CO)_{11}]^-$ are known entities [1,2,3]. However, only the one dianion $[Fe_3(CO)_{11}]^{2-}$ has been reported [4,5]. Described here are the preparation and isolation of the new dianions $[Ru_3(CO)_{11}]^{2-}$ and $[Os_3(CO)_{11}]^{2-}$.

We recently reported the preparation and isolation of salts of the tetranuclear anions $[Ru_4(CO)_{13}]^{2-}$ and $[Ru_4(CO)_{12}]^{4-}$, formed in high yields from stoichiometric reactions of potassium with $Ru_3(CO)_{12}$ in the presence of benzophenone as an electron carrier [6] (reactions 1 and 2).

$$4\ Ru_3(CO)_{12} + 6\ KPh_2CO \xrightarrow{THF} 3\ K_2[Ru_4(CO)_{13}] + 6\ Ph_2CO + 9\ CO \quad (1)$$

$$4\ Ru_3(CO)_{12} + 12\ KPh_2CO \xrightarrow{THF} 3\ K_4[Ru_4(CO)_{12}] + 12\ CO + 12\ Ph_2CO \quad (2)$$

However, we failed to isolate pure $K_2[Ru_3(CO)_{11}]$ from a reaction which employed a 1/2 molar ratio of $Ru_3(CO)_{12}$ to benzophenonepotassium. Instead, a mixture of primarily $K_2[Ru_4(CO)_{13}]$ and small amounts of $K_2[Ru_6(CO)_{18}]$ and $K_2[Ru_3(CO)_{11}]$, subsequently identified, was obtained. In the procedure employed it seems likely that the intermediate anion $[Ru_3(CO)_{11}]^{2-}$ is formed initially and that it interacts with $Ru_3(CO)_{12}$ to form the higher nuclearity anions. In order to minimize such subsequent reactions of $[Ru_3(CO)_{11}]^{2-}$, a procedure was employed in which this anion. as it formed, precipitated from solution as the calcium salt.

A glyme solution of calcium-benzophenone reacts with $Ru_3(CO)_{12}$ in a 1/1 molar ratio at ambient temperature according to reaction 3 (190 mg $Ru_3(CO)_{12}$ 23.8 mg Ca, 108 mg benzophenone).

$$Ru_3(CO)_{12} + Ca \xrightarrow[\text{glyme}]{Ph_2CO} Ca[Ru_3(CO)_{11}] + CO \qquad (3)$$

The reaction is complete within 15 minutes, producing a bright orange precipitate and 80% of the theoretical amount of CO. Immediate filtration and washing affords $Ca[Ru_3(CO)_{11}]\cdot 2C_4H_{10}O_2$ in 71% yield. (Anal. Found: C, 28.10; H, 3.07; Ca, 4.78; Ru, 34.14. $CaRu_3(CO)_{11}$ calcd.: C, 27.44; H, 2.42; Ca, 4.82; Ru, 36.46%.) The orange powder is very air and water sensitive. It reacts with one equivalent of HCl to form $[HRu_3(CO)_{11}]^-$. Its infrared spectrum as a Nujol mull exhibits a strong bridging carbonyl absorption at 1565 cm^{-1} as well as an absorption at 1065 cm^{-1} for the coordinated glyme.

It was also of interest to carry out benzophenonepotassium reductions of $Os_3(CO)_{12}$ in the same manner as $Ru_3(CO)_{12}$ has been reduced in this laboratory. In this case, we find that clusters of higher nuclearity are not formed in significant amounts. However, $[Os_3(CO)_{11}]^{2-}$ is readily formed and isolated as the potassium salt.

Reaction of potassium benzophenone with $Os_3(CO)_{12}$ proceeds at room temperature over a 3 h period according to reaction (60 mg $Os_3(CO)_{12}$, 5.3 mg K, 24.0 mg Ph_2CO).

$$Os_3(CO)_{12} + 2K \xrightarrow[\text{THF}]{Ph_2CO} K_2[Os_3(CO)_{11}] + CO \qquad (4)$$

Complete consumption of the relatively insoluble $Os_3(CO)_{12}$ occurs to produce a yellow-orange solution and 100% of the theoretical amount of CO evolution. Precipitation of the salt from a Me_2O/CH_2Cl_2 solution and washing with CH_2Cl_2 affords $K_2[Os_3(CO)_{11}]$ as a bright yellow-orange powder in 79% yield. (Anal. Found: C, 13.60; K, 8.62; Os, 59.27. $K_2[Os_3(CO)_{11}]$: calcd.: C, 13.80; K 8.17; Os, 59.62%.) It reacts with one equivalent of HCl to form $[HOs_3(CO)_{11}]^-$ The salt can also be metathesized to the $[Ph_4As]^+$ salt using $[Ph_4As]Cl$.

The infrared spectrum of $K_2[Os_3(CO)_{11}]$ in THF displays a bridging carbonyl absorption at 1625 cm^{-1} which is unchanged upon metathesis to the $[Ph_4As]^+$ salt [7]. A structure containing a single carbonyl bridge, as shown in Fig. 1, is suggested and is confirmed by low temperature ^{13}C NMR spectra recorded in $(CH_3)_2O/THF\text{-}d_8$ (2/1, v/v) on a sample prepared from 25% ^{13}C enriched $Os_3(CO)_{12}$. NMR spectra are also shown in Fig. 1. The slow exchange limit is not observed at the lowest temperature obtained, −138°C, however, the existence of a single bridging carbonyl is confirmed by the appearance of a low field signal with chemical shift 282.1 ppm, relative to TMS (δ 0 ppm). With this resonance assigned a relative intensity of one the remaining major peaks at 186.1 and 202.8 ppm integrate roughly as 8, and 2, respectively; thereby accounting for the 11 carbonyl groups in the formula. The peak of in-

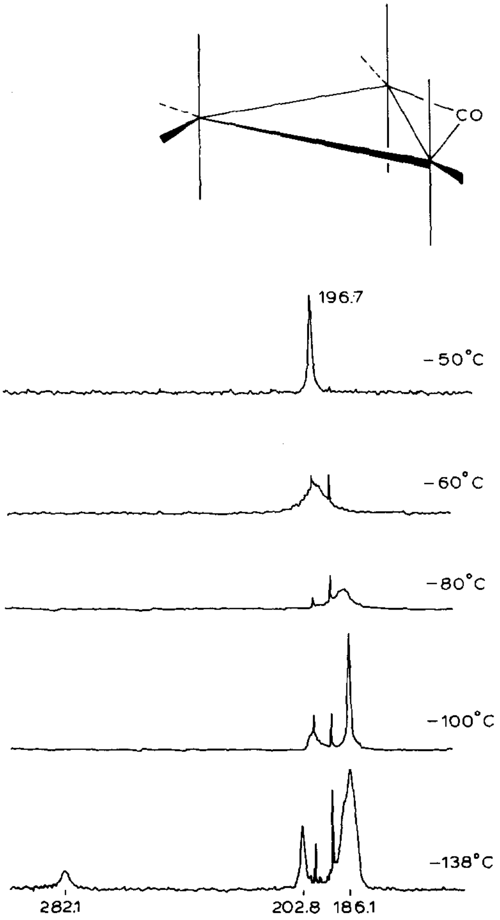
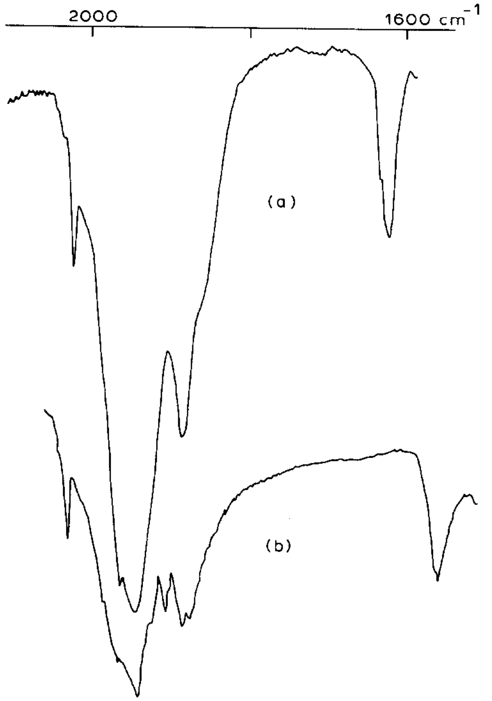


Fig. 1. Proposed structure of $[Os_3(CO)_{11}]^{2-}$ and the variable temperature 22.62 MHz carbon-13 NMR spectrum of $K_2[Os_3(CO)_{11}]$ in THF-d_8/Me_2O (25% ^{13}C enriched).

tensity 8 at 186.1 ppm is still broad. Upon warming the sample, the bridge signal disappears and, at −100°C, the peak at 186.1 ppm is sharp, indicating a process in which about half of the carbonyls are exchange averaging. Two small sharp peaks at 193 and 198 ppm appear to be temperature invariant and are believed to belong to impurities, probably osmium carbonylates of higher nuclearities. At higher temperature, there is coalescence of all peaks to give a single resonance at 196.7 ppm, in good agreement with the weighted average, 197.8 ppm. Thus spectral characterization is consistent with the proposed structure shown above which contains a single edge bridging carbonyl group.

Comparison of the infrared spectrum (Fig. 2) of $K_2[Os_3(CO)_{11}]$ with that of $Ca[Ru_3(CO)_{11}] \cdot C_4H_{10}O_2$ reveals several points of similarity. In the terminal carbonyl stretching region, both anions show a sharp absorption at about 2040 cm^{-1}, and a very strong, broad stretch at approximately 1950 cm^{-1} with a shoulder at 1880 cm^{-1}. The bridging region for both anions consists of a single, strong absorption. It is suggested that these trinuclear cluster dianions have similar structures.



ν(CO) cm^{-1}	
2040	m
1970	s
1950	vs
1890	m(sh)
1625	m
2042	s
1935	vs(br)
1903	m
1880	m
1870	m(sh)
1565	s

Fig. 2. (a) Infrared spectrum of $K_2[Os_3(CO)_{11}]$ in THF.
(b) Infrared spectrum of $Ca[Ru_3(CO)_{11}]$ as a Nujol mull.

Another reasonable approach to the syntheses of $[Os_3(CO)_{11}]^{2-}$ and $[Ru_3(CO)_{11}]^{2-}$ would be deprotonation [8] of $[HOs_3(CO)_{11}]^-$ and $[HRu_3(CO)_{11}]^-$, respectively. Deprotonation of $K[HOs_3(CO)_{11}]$ with KH produces mainly $K_2[Os_3(CO)_{11}]$ and 80% of the theoretical H_2 is evolved, but the $K_2Os_3(CO)_{11}$ is not pure. Attempts to deprotonate $K[HRu_3(CO)_{11}]$ with KH failed to yield the desired $K_2[Ru_3(CO)_{11}]$; only decomposition products were observed. Thus reduction of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ appears to be the preferred method for preparation of $[Os_3(CO)_{11}]^{2-}$ and $[Ru_3(CO)_{11}]^{2-}$.

Acknowledgement. We thank the National Science Foundation for support of this work through Grant No. CHE-791848. J.C.B. thanks the Graduate School of The Ohio State University for a Fellowship.

References

1 W. Hieber and G. Brendel, Z. Anorg. Chem., 289 (1957) 324.
2 B.F.G. Johnson, J. Lewis, P.R. Raithby and G. Suss, J. Chem. Soc., Dalton, (1979) 1356.
3 C.R. Eady, B.F.G. Johnson, J. Lewis, and M.C. Malatesta, J. Chem. Soc., Dalton, (1978) 1358.
4 W. Hieber, J. Sedlmeier, and R. Werner, Chem. Ber., 90 (1957) 278.
5 Evidence for the existence of the radical species $[Fe_3(CO)_{11}]^{\cdot}$ and $[HFe_3(CO)_{11}]^{\cdot}$ has recently been reported. P.J. Krusic; J.S. Filippo, Jr.; B. Hutchinson, R.L. Hance, and L.M. Daniels, J. Amer. Chem. Soc., 103 (1981) 2129. P.J. Krusic, ibid., 103 (1981) 2131.
6 C.C. Nagel and S.G. Shore, J. Chem. Soc. Chem. Comm., (1980) 530.
7 A similar low frequency bridge absorption has been observed for the isoelectronic $[H_2Os_3(CO)_{10}]^{2-}$ ion, which also has a single edge-bridging carbonyl. S. Kennedy and S.G. Shore, J. Organometal. Chem., in press.
8 K.E. Inkrott and S.G. Shore, Inorg. Chem., 18 (1979) 2817.