

Highly Reduced Organometallics. 10.¹ Synthesis and Chemistry of the Pentacarbonylmetallate(3-) Ions of Niobium and Tantalum, $M(\text{CO})_5^{3-}$

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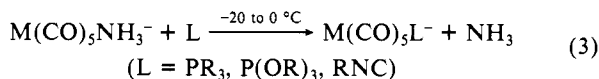
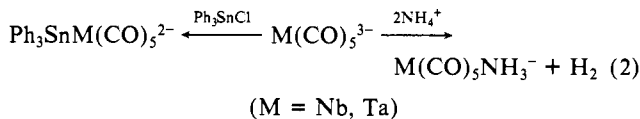
In this paper we report on the syntheses and characterizations of the pentacarbonylmetallate trianions of niobium and tantalum, which are the first compounds to contain these elements in a formal oxidation state of -3. Although metal carbonyl trianions of other second- and third-row transition elements have been claimed,² these are also the first examples to have been isolated as analytically pure substances.

Substantial differences in the carbonyl chemistry of first-row transition metals and that of second and third row homologues are often observed. For example, while $\text{Cr}(\text{CO})_6$ readily reacts with Na-NH_3 to provide high yields of $\text{Na}_2\text{Cr}(\text{CO})_5$, corresponding reductions of $M(\text{CO})_6$ ($M = \text{Mo}, \text{W}$) give only very low yields of thermally unstable $\text{Na}_2M(\text{CO})_5$.^{3,4} For these reasons it was by no means obvious whether reductions of the isoelectronic $M(\text{CO})_6^-$ ($M = \text{Nb}, \text{Ta}$) would provide species analogous to the previously reported $\text{V}(\text{CO})_5^{3-}$.⁵

Unlike the Na-NH_3 reductions of $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$, however, $[\text{Na}(\text{diglyme})_2][M(\text{CO})_6]^-$ are smoothly reduced by 3 equiv of sodium in liquid ammonia at -78°C to provide deep red solutions containing thermally unstable $\text{Na}_3[M(\text{CO})_5]$, according to eq 1. After filtration and cation exchange, deep red ($M = \text{Nb}$) or deep brown-red ($M = \text{Ta}$), slightly soluble, and apparently amorphous solids are obtained in 40–50% yields, which provide satisfactory analyses for unsolvated $\text{Cs}_3[M(\text{CO})_5]$.⁷ These materials have infrared spectra that are nearly superimposable on those of $\text{Cs}_3[\text{V}(\text{CO})_5]$.⁵ Although they appear to be only slightly less thermally stable than the vanadium analogue, as dry solids they are much more shock sensitive. One sample of $\text{Cs}_3[\text{Ta}(\text{CO})_5]$ exploded on standing at room temperature under an inert atmosphere. In this respect they resemble the unstable $\text{K}_3[\text{V}(\text{CO})_5]$.⁵ For these reasons, their chemical studies have been largely limited to the reactions of $M(\text{CO})_5^{3-}$ formed in situ in liquid ammonia.

Treatment of liquid ammonia solutions of $\text{Na}_3[M(\text{CO})_5]$ dropwise with 1 equiv of Ph_3SnCl in THF provides, after metathesis, 70–80% yields of orange to orange-red, crystalline $[\text{Et}_4\text{N}]_2[\text{Ph}_3\text{SnM}(\text{CO})_5]$.⁸ These oxygen-sensitive materials have infrared spectra in the $\nu(\text{CO})$ region that are consistent with the presence of a substituted dianion of C_{4v} symmetry.⁸ Also, nearly quantitative yields of the previously unknown $\text{Na}[M(\text{CO})_5\text{NH}_3]$ are obtained from the reaction of $\text{Na}_3[M(\text{CO})_5]$ with ammonium chloride in liquid ammonia. Although the sodium salts are thermally unstable, 40–45% yields of red violet ($M = \text{Nb}$) to deep

violet ($M = \text{Ta}$) crystalline $[\text{Ph}_4\text{As}][M(\text{CO})_5\text{NH}_3]$ may be obtained by metathesis.⁹ These ammine complexes, like their vanadium analogue,¹⁰ are very labile in solution and readily react at -20 to 0°C with a variety of π -acceptor ligands such as PR_3 , $\text{P}(\text{OR})_3$, and RNC to provide 50–80% isolated yields of the corresponding $M(\text{CO})_5\text{L}^-$. For example, the first isocyanide derivatives of tantalum and niobium carbonyls were obtained by treating ammonia solutions of $\text{Na}[M(\text{CO})_5\text{NH}_3]$ with *t*-BuNC followed by cation exchange and crystallization. Orange $[\text{Et}_4\text{N}][M(\text{CO})_5\text{CN-}t\text{-Bu}]$ were thereby obtained in 50–60% yields.¹¹ The chemistry of $M(\text{CO})_5^{3-}$ reported herein is summarized in eq 2 and 3.



It is anticipated that the carbonyl trianions of niobium and tantalum will be especially important as precursors to new metal clusters containing these elements. Studies in this latter area are in progress.

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(9) Anal. Calcd for $\text{C}_{29}\text{H}_{23}\text{O}_5\text{AsNNb}$: C, 55.26; H, 3.20; N, 2.22. Found: C, 55.13; H, 3.26; N, 2.34. IR ($\nu(\text{CO})$, Nujol) 1963 m, 1781 vs (br), 1759 vs (br) cm^{-1} . Anal. Calcd for $\text{C}_{29}\text{H}_{23}\text{O}_5\text{AsNTa}$: C, 48.49; H, 2.81; N, 1.95. Found: C, 48.03; H, 2.91; N, 1.90. IR ($\nu(\text{CO})$, Nujol) 1960 m, 1775 s (br), 1755 vs (br) cm^{-1} .

(10) (a) Ellis, J. E.; Fjare, K. L. *Organometallics* **1982**, *1*, 898. (b) Fjare, K. L.; Ellis, J. E. *Ibid.* **1982**, *1*, 1373.

(11) Anal. Calcd for $\text{C}_{18}\text{H}_{29}\text{N}_3\text{NbO}_5$: C, 48.44; H, 6.55; N, 6.28. Found: C, 48.21; H, 6.75; N, 6.23. IR (CH_3CN) ($\nu(\text{CN})$) 2090 w, $\nu(\text{CO})$: 1966 m, 1830 s cm^{-1} ; $^1\text{H NMR}$ (CD_3CN) δ 1.46 s (9 H) (Et_4N^+ signals omitted). Anal. Calcd for $\text{C}_{18}\text{H}_{29}\text{N}_3\text{TaO}_5$: C, 40.46; H, 5.47. Found: C, 40.79; H, 5.53. IR (CH_3CN) ($\nu(\text{CN})$) 2090 w, $\nu(\text{CO})$: 1960 m, 1828 s cm^{-1} ; $^1\text{H NMR}$ (CD_3CN) δ 1.48 s (9 H) (Et_4N^+ signals omitted).

Olefinic Cyclizations Promoted by Beckmann Rearrangement of Oxime Sulfonate

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The title reaction, if successful, would result in the direct formation of a wide variety of ring systems.¹⁻³

(1) For reviews of the Beckmann rearrangement, see: Blatt, A. H. *Chem. Rev.* **1933**, *12*, 215. Jones, B. *Chem. Rev.* **1944**, *35*, 335. Moller, F. In "Methoden der Organischen Chemie"; Müller, E., Ed.; Thieme Verlag: Stuttgart, 1957; Vol. XI, Part 1, p 892. Donaruma, I. G.; Heldt, W. Z. *Org. React. (N.Y.)* **1960**, *11*, 1. Beckwith, A. L. J. In "The Chemistry of Amides"; Zabicky, J., Ed.; Interscience: New York, 1970; p 131. McCarty, C. G. In "Chemistry of the Carbon-Nitrogen Double Bond"; Patai, S., Ed.; Wiley-Interscience: New York, 1970; p 408.

(2) The present rearrangement-cyclization process may proceed via nitrilium ions as intermediates, which can also be generated by the Ritter reaction. For an excellent review of the Ritter reaction, see: Meyers, A. I.; Sircar, J. C. In "The Chemistry of Cyano Group"; Rappoport, Z., Ed.; Interscience: New York, 1970; p 341. See also: Johnson, F.; Madronero, R. In "Advances in Heterocyclic Chemistry"; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1966; Vol. 6, p 95. Krimen, L. I.; Cota, D. J. *Org. React. (N.Y.)* **1969**, *17*, 213. Meyers, A. I.; Singh, H. J. *Org. Chem.* **1968**, *33*, 2365. Shome, M.; Smith, P. W.; Southam, R. M.; Oxford, A. W. *Tetrahedron Lett.* **1980**, *21*, 2927.

(1) Part 9: Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.*, in press.

(2) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, 686 and references cited therein.

(3) Behrens, H. *Adv. Organomet. Chem.* **1980**, *18*, 2.

(4) Maher, J.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1982**, *1*, 215.

(5) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100.

(6) Dewey, C. G.; Ellis, J. E.; Fjare, K. L.; Pfahl, K. M.; Warnock, G. F. *Organometallics*, in press.

(7) Anal. Calcd for $\text{C}_5\text{Cs}_3\text{NbO}_5$: C, 9.61; Cs, 63.12; H, 0.00. Found: C, 9.47; Cs, 63.35; H, 0.07. IR Nujol, ($\nu(\text{CO})$ region) 1810 w (sharp), 1566 vs. (br) cm^{-1} . Anal. Calcd for $\text{C}_5\text{Cs}_3\text{TaO}_5$: C, 8.34; Cs, 55.40; Ta, 25.14; H, 0.00. Found: C, 8.23; Cs, 55.68; Ta, 25.03; H, 0.12. IR Nujol, ($\nu(\text{CO})$ region) 1813 w (sharp), 1562 vs (br) cm^{-1} .

(8) Anal. Calcd for $\text{C}_{39}\text{H}_{55}\text{N}_2\text{O}_5\text{SnTa}$: C, 50.29; H, 5.95; N, 3.01. Found: C, 49.95; H, 5.83; N, 3.03. IR ($\nu(\text{CO})$, in CH_3CN) 1942 m, 1785 vs, 1755 sh cm^{-1} . Anal. Calcd for $\text{C}_{39}\text{H}_{55}\text{N}_2\text{O}_5\text{NbSn}$: C, 55.54; H, 6.57; N, 3.32. Found: C, 55.42; H, 6.48; N, 3.45. IR ($\nu(\text{CO})$, CH_3CN) 1948 m, 1790 vs, 1750 sh cm^{-1} . $^1\text{H NMR}$ spectra in CD_3CN show integrations of phenyl and ethyl protons that are consistent with these formulations.