Highly Reduced Organometallics. 10.[1] Synthesis and Chemistry of the Pentacarbonylmetallate(3–) Ions of Niobium and Tantalum, $M(CO)_5^{3-}$

Garry F. P. Warnock, Julian Sprague, Kristi L. Fjare, and John E. Ellis*

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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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 $Cr(CO)_6$ readily reacts with Na–NH_3 to provide high yields of $Na_2Cr(CO)_5$, corresponding reductions of $M(CO)_6$ (M = Mo, W) give only very low yields of thermally unstable $Na_2M(CO)_5$.[3,4] For these reasons it was by no means obvious whether reductions of the isoelectronic $M(CO)_6^-$ (M = Nb, Ta) would provide species analogous to the previously reported $V(CO)_5^{3-}$.[5]

Unlike the Na–NH_3 reductions of $Mo(CO)_6$ and $W(CO)_6$, however, $[Na(diglyme)_2][M(CO)_6]$[6] are smoothly reduced by 3 equiv of sodium in liquid ammonia at −78° C to provide deep red solutions containing thermally unstable $Na_3[M(CO)_5]$, according to eq 1. After filtration and cation exchange, deep red (M = Nb) or deep brown-red (M = Ta), slightly soluble, and apparently amorphous solids are obtained in 40–50% yields, which provide satisfactory analyses for unsolvated $Cs_3[M(CO)_5]$.[7] These materials have infrared spectra that are nearly superimposable on those of $Cs_3[V(CO)_5]$.[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 $Cs_3[Ta(CO)_5]$ *exploded* on standing at room temperature under an inert atmosphere. In this respect they resemble the unstable $K_3[V(CO)_5]$.[5] For these reasons, their chemical studies have been largely limited to the reactions of $M(CO)_5^{3-}$ formed in situ in liquid ammonia.

$$Na[M(CO)_6] + 3Na \rightarrow Na_3[M(CO)_5] + {}^1/_2[Na_2C_2O_2]\downarrow \quad (1)$$

Treatment of liquid ammonia solutions of $Na_3[M(CO)_5]$ dropwise with 1 equiv of Ph_3SnCl in THF provides, after metathesis, 70–80% yields of orange to orange-red, crystalline $[Et_4N]_2[Ph_3SnM(CO)_5]$.[8] These oxygen-sensitive materials have infrared spectra in the ν(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 $Na[M(CO)_5NH_3]$ are obtained from the reaction of $Na_3[M(CO)_5]$ with ammonium chloride in liquid ammonia. Although the sodium salts are thermally unstable, 40–45% yields of red violet (M = Nb) to deep violet (M = Ta) crystalline $[Ph_4As][M(CO)_5NH_3]$ 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, $P(OR)_3$, and RNC to provide 50–80% isolated yields of the corresponding $M(CO)_5L^-$. For example, the first isocyanide derivatives of tantalum and niobium carbonyls were obtained by treating ammonia solutions of $Na[M(CO)_5NH_3]$ with *t*-BuNC followed by cation exchange and crystallization. Orange $[Et_4N][M(CO)_5CN\text{-}t\text{-}Bu]$ were thereby obtained in 50–60% yields.[11] The chemistry of $M(CO)_5^{3-}$ reported herein is summarized in eq 2 and 3.

$$Ph_3SnM(CO)_5^{2-} \xleftarrow{Ph_3SnCl} M(CO)_5^{3-} \xrightarrow{2NH_4^+} M(CO)_5NH_3^- + H_2 \quad (2)$$

$$(M = Nb, Ta)$$

$$M(CO)_5NH_3^- + L \xrightarrow{-20 \text{ to } 0\ °C} M(CO)_5L^- + NH_3 \qquad (3)$$

$$(L = PR_3, P(OR)_3, RNC)$$

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

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(7) Anal. Calcd for $C_5Cs_3NbO_5$: C, 9.61; Cs, 63.12; H, 0.00. Found, C, 9.47; Cs, 63.35; H, 0.07. IR Nujol, (ν(CO) region) 1810 w (sharp), 1566 vs. (br) cm^{-1}. Anal. Calcd for $C_5Cs_3O_5Ta$: 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, (ν(CO) region) 1813 w (sharp), 1562 vs (br) cm^{-1}.

(8) Anal. Calcd for $C_{39}H_{55}N_2O_5SnTa$: C, 50.29; H, 5.95; N, 3.01. Found: C, 49.95; H, 5.83; N, 3.03. IR (ν(CO), in CH_3CN) 1942 m, 1785 vs, 1755 sh cm^{-1}. Anal. Calcd for $C_{39}H_{55}N_2O_5NbSn$: C, 55.54; H, 6.57; N, 3.32. Found: C, 55.42; H, 6.48; N, 3.45. IR (ν(CO), CH_3CN) 1948 m, 1790 vs, 1750 sh cm^{-1}. ^{1}H NMR spectra in CD_3CN show integrations of phenyl and ethyl protons that are consistent with these formulations.

(9) Anal. Calcd for $C_{29}H_{23}O_5AsNNb$: C, 55.26; H, 3.20; N, 2.22. Found: C, 55.13; H, 3.26; N, 2.34. IR (ν(CO), Nujol) 1963 m, 1781 vs (br), 1759 vs (br) cm^{-1}. Anal. Calcd for $C_{29}H_{23}O_5AsNTa$: C, 48.49, H, 2.81; N, 1.95. Found: C, 48.03; H, 2.91; N, 1.90. IR (ν(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 $C_{18}H_{29}N_2NbO_5$: C, 48.44; H, 6.55; N, 6.28. Found: C, 48.21; H, 6.75; N, 6.23. IR (CH_3CN) (ν(CN)) 2090 w, ν(CO): 1966 m, 1830 s cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.46 s (9 H) (Et_4N^+ signals omitted). Anal. Calcd for $C_{18}H_{29}N_2O_5Ta$: C, 40.46; H, 5.47. Found: C, 40.79; H, 5.53. IR (CH_3CN) (ν(CN)) 2090 w, (ν(CO)) 1960 m, 1828 s cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.48 s (9 H) (Et_4N^+ signals omitted).

Olefinic Cyclizations Promoted by Beckmann Rearrangement of Oxime Sulfonate

Soichi Sakane, Yasushi Matsumura, Yoshihiro Yamamura, Yasuko Ishida, Keiji Maruoka, and Hisashi Yamamoto*

Department of Applied Chemistry, Nagoya University
Chikusa, Nagoya 464, Japan

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

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(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.

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