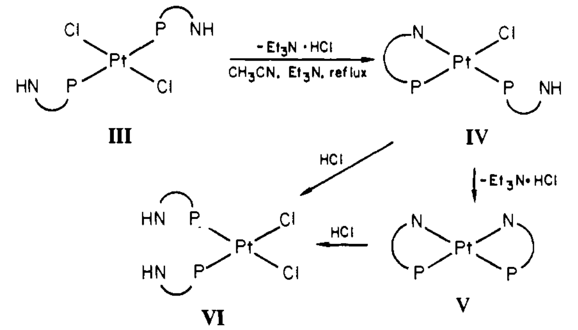
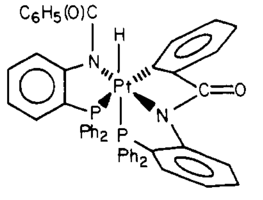
Scheme I[a]



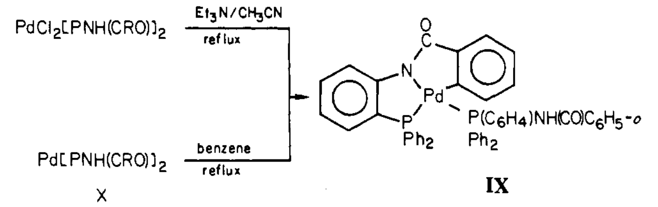
[a] $\widehat{\mathrm{P\,NH}}$ = o-$Ph_2PC_6H_4NHC(O)C_6H_5$; $\widehat{\mathrm{P\,N}}$ = o-$Ph_2PC_6H_4NC(O)C_6H_5^-$.

o-$Ph_2PC_6H_4NHC(O)C_6D_5$ has been prepared from o-$Ph_2PC_6H_4NH_2$ and C_6D_5COCl. Isolation of VII using this ligand yields a product deuterated at nitrogen (ν_{ND} 2260 cm^{-1}). This result suggests conversion of V to VII via C–H addition followed by N–H reductive elimination from the platinum(IV) hydride intermediate VIII.[7,20]



VIII

The palladium analogue IX is formed in high yield from $PdCl_2[PNH(CRO)]_2$ and Et_3N in acetonitrile. Alternatively, IX can be prepared by refluxing a benzene suspension of the complex $Pd[PNH(CRO)]_2$ (X).



Acknowledgment. We thank B. Brammel (U.N.O.) for ^1H NMR measurements and U. Geiser (W.S.U.) for magnetic measurements. We thank the Colorado State University Regional NMR Center, funded by National Science Foundation Grant CHE-820882, for the 360-MHz ^1H NMR spectrum. The University of Delaware received support from the National Science Foundation for the purchase of the diffractometer.

Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic temperature factors, and hydrogen atom coordinates for VII, and microanalytical and IR and NMR spectral data for all new compounds (41 pages). Ordering information is given on any current masthead page.

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[19] For VII: space group $P\bar{1}$, a = 12.038 (3) Å, b = 12.576 (5) Å, c = 16.220 (6) Å, α = 105.80 (3)°, β = 104.84 (3)°, γ = 95.75 (3)°, V = 2245.6 (13) Å^3, Z = 2. The structure was solved by standard heavy-atom methods and after correction for absorption was refined by blocked-cascade procedures (SHELXTL 4.1) with anisotropic temperature factors and rigid-body constraints on the terminal phenyl rings (5115 reflections, $3\sigma(F)$ cutoff). R_F = 3.75%, R_{wF} = 4.02%. A severely disordered, substoichiometric (site occupation ~20%) molecule of $CHCl_3$ was found and refined.

[20] (a) Blacklaws, I. M.; Brown, L. C.; Ebsworth, E. A. V.; Reed, F. J. S. *J. Chem. Soc., Dalton Trans.* **1978**, 877–879. (b) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Wiley: New York, 1979; Chapter 18.

Highly Reduced Organometallics. 17. Synthesis, Isolation, and Characterization of Hydridopentacarbonylmetalate(2–) Anions of Vanadium, Niobium, and Tantalum: $HM(CO)_5^{2-}$

Garry F. P. Warnock and John E. Ellis*

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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Compounds of the general formula $HM(CO)_x^{2-}$ have been postulated to be key intermediates in the reactions of carbonylmetalate trianions, $M(CO)_x^{3-}$, with Brønsted acids, but very little evidence for their existence has been presented previously.[2,3] In this communication, the isolation and characterization of monoprotonated derivatives of the carbonyl trianions of vanadium, niobium, and tantalum are described. These are the first examples of hydrides containing transition metals in formally negative oxidation states. Their synthesis also provides important additional evidence for the existence of unprotonated carbonyl trianions since the latter have been previously characterized mainly on the basis of their derivative chemistry.[2,4] It is well established that carbonyl hydrides and their conjugate bases often cannot be distinguished reliably on this basis.[5]

Treatment of the rea to deep red ammoniacal solutions of $Na_3[M(CO)_5]$ (M = V,[2] Nb,[4] and Ta[4]) dropwise with 1 equiv of ethanol in THF at –70 °C over a period of 5 min provided orange to red-orange solutions. Addition of 3 equiv of $[Et_4N][BH_4]$ at –70 °C resulted in the rapid precipitation of 60–80% yields of microcrystalline bright yellow (**1**, V), orange (**2**, Nb), or orange-red (**3**, Ta) products. These air-sensitive solids provided satisfactory elemental analyses for unsolvated $[Et_4N]_2[HM(CO)_5]$ without further purification.[6] Infrared spectra for compounds **1**–**3**[7] were qualitatively very similar to those of the corresponding triphenylstannyl substituted dianions, $[Et_4N]_2[Ph_3SnM(CO)_5]$.[2,4] However, it was necessary to obtain NMR spectra of these substances to exclude alternative formulations such as $[Et_4N]_4[M_2(CO)_{10}]$. These spectra had to be obtained for the thermally unstable disodium salts, $Na_2[HM(CO)_5]$, in *liquid ammonia* at –50 °C because of facile decomposition of compounds **1**–**3** in polar solvents at room temperature and their poor solubility at low temperatures. The ^1H NMR spectrum for $Na_2[HTa(CO)_5]$ exhibited a fairly sharp singlet ($\Delta\nu_{1/2}$ = 30 Hz) at –2.23 ppm which is compatible with previous values reported for the isoelectronic species $HW(CO)_5^-$ (–4.2 ppm)[8] and $HRe(CO)_5$ (–5.7 ppm).[9] Initial attempts to detect the hydride resonance of $Na_2[HNb(CO)_5]$ were unsuccessful.[10]

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[1] Part 16: Pfahl, K. M.; Ellis, J. E. *Organometallics* **1984**, *3*, 230.

[2] Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100.

[3] Ellis, J. E.; Fjare, K. L. *Organometallics* **1982**, *1*, 898. Fjare, K. L.; Ellis, J. E. *Ibid.* **1982**, *1*, 1373.

[4] Warnock, G. F. P.; Sprague, J.; Fjare, K. L.; Ellis, J. E. *J. Am. Chem. Soc.*, **1983**, *105*, 672.

[5] A recent example: Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500.

[6] Anal. Calcd for **1**, $C_{21}H_{41}N_2O_5V$: C, 55.74; H, 9.13; N, 6.19. Found: C, 55.51; H, 8.90; N, 6.06. Anal. Calcd for **2**, $C_{21}H_{41}N_2NbO_5$: C, 51.01; H, 8.36; N, 5.66. Found: C, 51.33; H, 8.21; N, 5.56. Anal. Calcd for **3**, $C_{21}H_{41}N_2O_5Ta$: C, 43.30; N, 7.09; N, 4.81. Found: C, 43.26; H, 6.69; N, 4.77.

[7] Nujol mull spectra in ν(CO) region for **1**: 1905 w, 1700 s, br. **2**: 1923 w, 1700 s, br. **3**: 1922 w, 1700 s, br. Metal-hydride stretching frequencies have not been identified for these compounds.

[8] Darensbourg, M. Y.; Slater, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 5914.

[9] Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Am. Chem. Soc.* **1963**, 1133.

[10] Several other groups have reported difficulties in observing niobium hydrides by NMR: Labinger, J. A. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., eds.; Pergamon Press: New York, 1982; Vol. 3, p 707. Also see ref 1.

However, the ^{93}Nb NMR spectrum (73.29 MHz) for this substance was easily obtained (−2122 ppm, br d, J_{Nb-H} = ca. 80 Hz).[11] A sharp hydride signal was then seen at −1.89 ppm in the ^{1}H{^{93}Nb} NMR spectrum of $Na_2[HNb(CO)_5]$ (cf. −4.0 ppm for $HMo(CO)_5^-$).[8]

Proton and ^{51}V NMR spectral studies on the protonation of $Na_3[V(CO)_5]$ in liquid ammonia have proven to be particularly informative. While a freshly prepared solution of $Na_3[V(CO)_5]$ showed no metal hydride signals in its ^{1}H NMR spectrum, the ^{51}V NMR spectrum of this substance exhibited a well-resolved singlet at −1962 ppm ($\Delta\nu_{1/2}$ = 18 Hz).[12] Treatment of $Na_3[V(CO)_5]$ with less than 1 equiv of EtOH at −50 °C caused reduction in the intensity of the signal assigned to the trianion while a sharp doublet (J_{V-H} = 27.6 Hz, $\Delta\nu_{1/2}$ = 8 Hz) grew in at −1986 ppm (see Figure 1). The corresponding ^{1}H NMR spectrum of this monoprotonated species (see Figure 2) showed a well-resolved octet (J_{V-H} = 27.6 Hz) centered at −4.76 ppm (cf. −6.9 ppm for $HCr(CO)_5^-$)[13] due to the coupling of *one* vanadium (^{51}V is 99.76% abundant, $I = {}^{7}/_{2}$) to hydrogen.[14] These spectra indicate that a mononuclear vanadium monohydride is present and are consistent with the formulation $HV(CO)_5^{2-}$. Addition of more than 1 equiv of ethanol to $Na_3[V(CO)_5]$ caused the singlet at −1962 ppm to diminish and the doublet at −1986 to become less intense. A new and rather broad signal at −1604 ppm ($\Delta\nu_{1/2}$ = 70 Hz) due to $V(CO)_5NH_3^-$[2,3,15] had grown in. Interestingly, except for small amounts of $V(CO)_6^-$ (see Figure 1), the only vanadium compounds observed during these protonation reactions were $V(CO)_5^{3-}$, $HV(CO)_5^{2-}$, and $V(CO)_5NH_3^-$. If $H_3V(CO)_5$ or $H_2V(CO)_5^-$ did form during this reaction they must be relatively short lived at −50 °C in liquid ammonia. Similarly, we have no spectroscopic evidence for the formation of di- or trihydrides of niobium or tantalum during the protonations of the parent trianions or monohydrides.

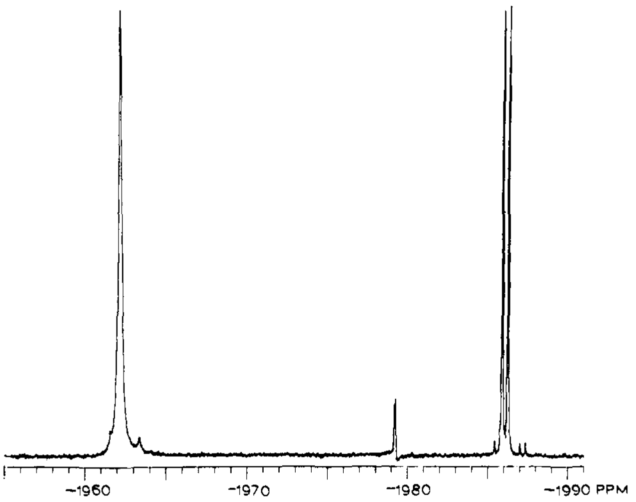

Figure 1. 77.87-MHz ^{51}V NMR spectrum of $Na_3[V(CO)_5]$, J(V–C) = 139 Hz, and $Na_2[HV(CO)_5]$, J(V–H) = 27.6 Hz, J(V–C) = 124.5 Hz, in liquid ammonia at −50 °C. The impurity at −1979 ppm is $V(CO)_6^-$.

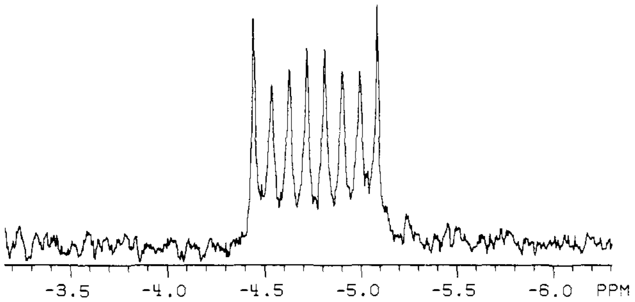

Figure 2. 300-MHz ^{1}H NMR spectrum of $Na_2[HV(CO)_5]$, J(V–H) = 27.6 Hz, in liquid ammonia at −50 °C.

The hydridopentacarbonylmetalate dianions readily transfer hydride ion to neutral metal carbonyls and in this respect resemble the group 6 monoanionic analogues $HM(CO)_5^-$ which Darensbourg and co-workers have studied extensively.[8,13,16] For example, suspensions of compounds **1–3** in THF rapidly react with $Fe(CO)_5$ at −50 °C to generate $M(CO)_5(THF)^-$[17] as well as $Fe(CO)_4CHO^-$ and $HFe(CO)_4^-$, where the former is the principal iron product.[18] However, while the group 6 monoanions, e.g., $HW(CO)_5^-$, are reasonably inert to acetonitrile,[8] the hydride dianions rapidly decompose in this medium at 25 °C to provide $M(CO)_5(CH_3CN)^-$, $M(CO)_6^-$, as well as another, as yet uncharacterized, carbonyl anion. Facile decomposition also occurs in dimethyl sulfoxide to provide the labile Me_2SO complexes, $M(CO)_5(Me_2SO)^-$.[19] Despite their high reactivity, however, compounds **1–3** are far less sensitive, more easily handled, and in some cases more useful as synthetic precursors than the parent trianions. For example, $[Et_4N]_2[HTa(CO)_5]$ reacts with 3 equiv of Ph_3PAuCl in THF at room temperature to provide approximately 60% yields of orange-red $(Ph_3PAu)_3Ta(CO)_5$[20] which is analogous to the known trigold–vanadium cluster $(Ph_3PAu)_3V(CO)_5$.[21]

$$3Ph_3PAuCl + HTa(CO)_5^{2-} \rightarrow (Ph_3PAu)_3Ta(CO)_5 + HCl + 2Cl^-$$

In contrast, none of this new gold–tantalum cluster could be obtained from the reaction of $Cs_3[Ta(CO)_5]$[4] and Ph_3PAuCl conducted under essentially identical conditions.

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(11) This value is relative to $NbCl_6^-$ in acetonitrile at 25 °C which is assigned a chemical shift of 0 ppm. In the liquid ammonia solution of $HNb(CO)_5^{2-}$, ^{93}Nb resonances due to $Nb(CO)_5NH_3^-$[4] (−1880 ppm, br) and $Nb(CO)_6^-$ (−2136 ppm, J_{Nb-C} = 236 Hz) were also observed. Our chemical shift for $Nb(CO)_6^-$ agrees well with that previously reported for $[Et_4N][Nb(CO)_6]$ in THF at −50 °C: Bechtold, H. C.; Rehder, D. *J. Organomet. Chem.* **1982**, *233*, 215.

(12) These values are relative to neat $VOCl_3$ at 25 °C which is assigned a chemical shift of 0 ppm. ^{51}V NMR spectra of several related substituted vanadium carbonyl anions have been reported recently: Talay, R.; Rehder, D. *J. Organomet. Chem.* **1984**, *262*, 25.

(13) Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* **1981**, *20*, 1644.

(14) A rather broad doublet (J_{V-H} = 20 Hz) has been observed in the ^{51}V NMR spectrum of $C_5H_5V(CO)_3H^-$. This appears to be the only other vanadium hydride for which ^{51}V–H coupling has been resolved. Puttfarcken, U.; Rehder, D. *J. Organomet. Chem.* **1980**, *185*, 219.

(15) (a) Rehder, D. *J. Organomet. Chem.* **1972**, *37*, 303. (b) Rehder, D.; Ihmels, K. *Inorg. Chim. Acta* **1983**, *76*, L313.

(16) Arndt, L.; Delord, T.; Darensbourg, M. *J. Am. Chem. Soc.* **1984**, *106*, 456 and references cited therein.

(17) These deep-purple and thermally unstable substituted anions have been generated independently by the photolysis of $M(CO)_6^-$ in THF at −78° C (Fjare, K. L.; Ellis, J. E., unpublished research; see also ref 15b for $V(CO)_5(THF)^-$). They react within 1–2h with PPh_3 at −50 to −60 °C to provide high yields of $M(CO)_5PPh_3^-$.[2–4]

(18) $[Et_4N][Fe(CO)_4CHO]$ and $[Et_4N][HFe(CO)_4]$ were identified by their characteristic proton chemical shifts at 25 °C of +14.8 ppm (Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089) and −8.8 ppm (Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119), respectively. NMR integration indicated the formyl:hydride ratio to be approximately 2:1 at −50 °C.

(19) The vanadium complex has been reported previously. Ihmels, K.; Rehder, D. *J. Organomet. Chem.* **1982**, *232*, 151.

(20) Anal. Calcd for $C_{59}H_{45}Au_3O_5P_3Ta$: C, 41.72; H, 2.67. Found: C, 41.59; H, 2.80. IR (THF) ν(CO): 1976 vs, 1829 w, 1855 s. ^{31}P{^{1}H} NMR (CH_2Cl_2): 56.5 ppm, s (relative to external H_3PO_4).

(21) Ellis, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 6106.