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# Characterization of Pentacarbonylvanadate(−III) and Hydridopentacarbonylvanadate(−II) by $^{13}$C, $^{51}$V, and $^{1}$H N.M.R. Spectroscopy

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N.m.r. spectra of highly reduced vanadium carbonyls containing 99% enriched $^{13}$CO in liquid ammonia at −50 °C provide the first direct spectroscopic evidence for the existence of $Na_3[V(CO)_5]$ and $Na_2[HV(CO)_5]$ in solution.

Although several mononuclear metal carbonyl trianions have been claimed in recent years, their formulations have been based only on elemental analyses, i.r. data, and derivative characterization.[1] Recently, $^{51}$V (77.87 MHz) and $^{13}$C (75.44 MHz) n.m.r. spectra of $Na_3[V(^{13}CO)_5]$, (**1**), in liquid ammonia have been obtained to clarify the nature of this unusual substance which formally contains vanadium in its lowest known oxidation state.[2] This n.m.r. study is particularly significant in that it provides the first direct evidence for the presence of $V(CO)_5{}^{3-}$ in solution.† Reduction of $[Na(diglyme)_2][V(^{13}CO)_6]$,‡ (**2**), by Na–NH$_3$ at −78 °C gave a characteristic deep red solution of $Na_3[V(CO)_5]$.[2] The $^{51}$V and $^{13}$C n.m.r. spectra of this solution indicated that the major species present was (**1**) along with small amounts of (**2**).§ As expected for a fluxional molecule with five co-ordination, five equivalent carbonyl groups are present. Also, the highly reduced nature of (**1**) is evident from the large (67.8 p.p.m.) downfield shift of its $^{13}$C resonance from that of (**2**). Similarly, $Na_2[W(CO)_5]$ has recently been shown to have a $^{13}$C resonance (δ 247.4, singlet in tetrahydrofuran) which is 55 p.p.m. downfield from the $W(CO)_6$ absorption.[4] To our knowledge, the $^{13}$C resonance of (**1**) is the most positive chemical shift yet observed for a terminal metal carbonyl group.

$Na_3[V(^{13}CO)_5]$ (**1**)

$[Na(diglyme)_2][V(^{13}CO)_6]$ (**2**)

$Na_2[HV(^{13}CO)_5]$ (**3**)

$V(^{13}CO)_5NH_3{}^-$ (**4**)

Treatment of liquid NH$_3$ solutions of (**1**) with one equiv. of ethanol at −50 °C caused reduction in the intensity of signals attributed to the trianion. New absorptions due to $Na_2[HV(^{13}CO)_5]$, (**3**), appeared.¶ The $^{51}$V and $^{13}$C{$^1$H}

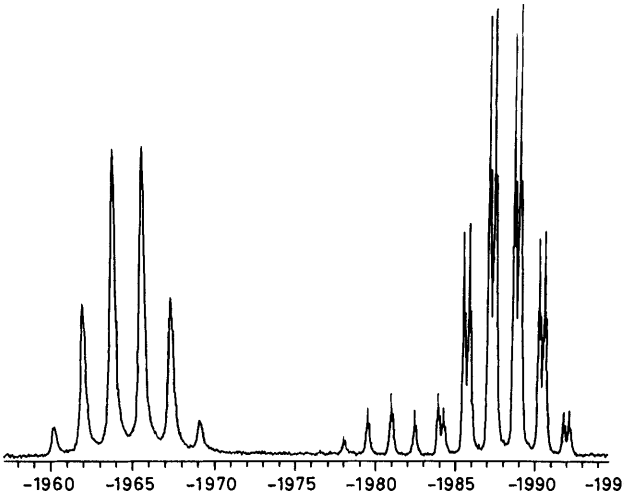

**Figure 1.** The $^{51}$V n.m.r. spectrum of $Na_3[V(^{13}CO)_5]$ (δ −1965 p.p.m.), $Na[V(^{13}CO)_6]$ (δ −1981 p.p.m.), and $Na_2[HV(^{13}CO)_5]$ (δ −1988 p.p.m.) in NH$_3$ at −50 °C. The satellites in the spectrum of $V(CO)_6{}^-$ and $HV(CO)_5{}^{2-}$ are due to *ca.* 10 mol % of co-ordinated $^{13}C^{18}O$.

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† All n.m.r. spectra reported herein were obtained for liquid NH$_3$ solutions at −50 °C; $^{51}$V n.m.r. chemical shifts were calibrated relative to neat VOCl$_3$ at 25 °C (0 p.p.m.) and $V(^{12}CO)_6{}^-$ in liquid NH$_3$ at −50 °C (−1979 p.p.m.). $^{13}$C N.m.r. shifts were calibrated relative to the carbon shifts of $Na(diglyme)_2{}^+$ in NH$_3$ at −50 °C and those of $Na(diglyme)_2{}^+$ and Me$_4$Si (0 p.p.m.) in [$^2$H$_6$]acetone at −50 °C. Diglyme = bis(2-methoxyethyl) ether.

‡ Compound (**2**) was prepared by a recently developed reductive carbonylation of VCl$_3$ (ref. 3) in the presence of 99% $^{13}$CO. I.r. (MeCN) ν(CO) 1818 cm$^{-1}$ [calculated ν($^{13}$CO) 1819 cm$^{-1}$ based on the observed ν($^{12}$CO) of 1860 cm$^{-1}$ for $V(^{12}CO)_6{}^-$]. N.m.r. in NH$_3$: $^{51}$V, δ −1981 p.p.m. [binomial septet, *J*(V–C) 116 Hz]; $^{13}$C, δ 224.2 [octet, *J*(V–C) 116 Hz].

§ N.m.r. data for (**1**) in NH$_3$: $^{51}$V, δ −1965 p.p.m. [binomial sextet, *J*(V–C) 139 Hz]; $^{13}$C, δ 290.1 p.p.m. [octet, *J*(V–C) 139 Hz].

¶ N.m.r. data for (**3**) in NH$_3$: $^{51}$V{$^1$H}, δ −1988 p.p.m. [binomial sextet, *J*(V–C) 124.5 Hz]; $^{51}$V, δ −1988 p.p.m. [sextet of doublets, *J*(V–C) 124.5, *J*(V–H) 27.6 Hz]; $^{13}$C{$^1$H}, δ 250.3 [octet, *J*(V–C) 124.5 Hz]. In another study $[Et_4N]_2[HV(CO)_5]$ was isolated as a yellow crystalline substance which provided satisfactory elemental analyses for this formulation (ref. 5). Compound (**3**) appears to be unstable above 0 °C in solution or in the solid state.

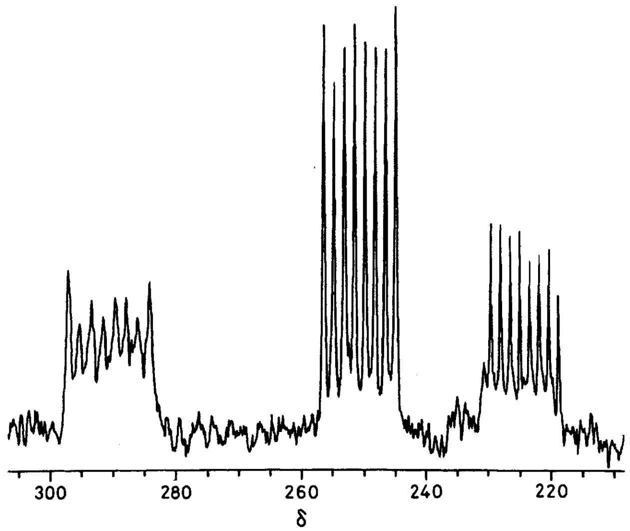

**Figure 2.** The $^{13}C\{^1H\}$ n.m.r. spectrum of $Na_3[V(^{13}CO)_5]$ (δ 290.1), $Na_2[HV(^{13}CO)_5]$ (δ 250.3), and $Na[V(^{13}CO)_6]$ (δ 224.2) in $NH_3$ at −50 °C.

n.m.r. spectra (Figures 1 and 2, respectively) established the presence of (**1**), (**2**), and (**3**) in this solution. The resonances due to these species in the $^{13}C$ n.m.r. spectrum were unambiguously identified on the basis of their respective $^{51}V$–$^{13}C$ coupling constants. Confirmation of the hydridic and mononuclear nature of (**3**) was provided by its $^1H$ n.m.r. spectrum (300 MHz) in $NH_3$ at −50 °C: δ −4.78 [partially overlapped sextet of octets, *J*(V–H) 27.7, *J*(C–H) 10.8 Hz]. From the $^{51}V$, $^{13}C$, and $^1H$ n.m.r. spectra of (**3**), it is evident that the vanadium and hydrogen atoms are coupled to five equivalent carbon atoms at −50 °C in liquid $NH_3$. In this respect, the vanadium hydride resembles the isoelectronic chromium monoanion, $HCr(CO)_5^-$, which appears to be fluxional at 25 °C in acetonitrile.[6]

When the ammoniacal solution of (**1**) and (**3**) was treated with another equivalent of ethanol, n.m.r. absorptions due to these substances decreased in intensity while those due to a purple anion, $V(^{13}CO)_5NH_3^-$, (**4**) appeared and grew in intensity.** It is noteworthy that during this multinuclear n.m.r. study of the protonation of $V(^{13}CO)_5^{3-}$ in liquid ammonia, only the trianion, $HV(^{13}CO)_5^{2-}$, $V(^{13}CO)_5NH_3^-$, and small amounts of $V(^{13}CO)_6^-$ have been observed. At present, there is no evidence for the formation of other plausible carbonylvanadium species such as $H_2V(CO)_5^-$, $H_3V(CO)_5$, $V_2(CO)_{10}^{4-}$, or $HV_2(CO)_{10}^{3-}$ in this system.

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** N.m.r. data for (**4**) in $NH_3$: $^{51}V$, δ −1605 p.p.m. [br. binomial sextet, *J*(V–C) 122.4 Hz]; $^{13}C\{^1H\}$, δ 225.3 [unresolved octet, *J*(V–C) *ca.* 121 Hz]. Addition of a stronger acid, such as $NH_4Cl$, caused signals due to (**1**) and (**3**) to completely disappear and provided mainly $V(CO)_5NH_3^-$ and small amounts of $V(CO)_6^-$. The ammine compound has been isolated previously from similar reactions as the $Ph_4As^+$ salt (ref. 2).