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A NEW ROUTE TO SUBSTITUTED VANADIUM CARBONYL ANIONS. SYNTHESES OF ALKYL AND ARYL ISOCYANIDEPENTACARBONYLVANADATE(1—) COMPLEXES, $V(CO)_5CNR^-$

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Summary

Aminepentacarbonylvanadate(1—) ion undergoes thermal substitution in the presence of π acceptor ligands to provide high yields (65—85%) of $V(CO)_5L^-$. By this method $[Et_4N][V(CO)_5Ph_2PCH_2PPh_2]$, containing an unligated PPh_2, $[Et_4N][V(CO)_5((p\text{-}ClC_6H_4)_3P)]$ and the first examples of the isocyanide substituted anions $[V(CO)_5CNR]^-$, where R = Me, t-Bu, cyclohexyl and phenyl have been prepared. This new method provides only monosubstituted carbonylvanadate(1—) ions and is especially important when such products are unavailable or not readily preparable by photochemical means.

Recent work by Adams [1—6] on isocyanide-substituted carbonyl anions has shown these materials to be highly reactive and useful precursors to a variety of novel materials. Several isocyanide substituted anions of $[Mn(CO)_5]^-$ and $[C_5H_5M(CO)_3]^-$ (M = Mo and W) have been prepared by the reduction of corresponding isocyanide metal carbonyl halides [1—6]. However, there exist no reports on similar substituted anions of $[V(CO)_6]^-$, in part, because isocyanide vanadium carbonyl halides are unknown.

Photosubstitution of phosphines and related ligands into $[V(CO)_6]^-$ has been the standard method for the synthesis of $[V(CO)_{6-x}L_x]^-$ (x = 1, 2, 3,; L = PR_3, AsR_3, etc.). [7—11]. Our attempts to extend this method to the preparation of $[V(CO)_5CNR]^-$ have been unsuccessful. However, recently we discovered that $[V(CO)_5NH_3]^-$ [8] readily undergoes thermal substitution in acetonitrile-ammonia or tetrahydrofuran from —20 to 0°C to give high isolated yields (80—85%) of new $[V(CO)_5PR_3]^-$, including yellow $[Et_4N][V(CO)_5Ph_2PCH_2PPh_2]$, which contains an unligated PPh_2 group as shown by ^{31}P NMR (Table 1 footnote *c*) and yellow $[Et_4N][V(CO)_5((p\text{-}ClC_6H_4)_3P)]$. Unsuccessful attempts to isolate these materials by the photolysis of $[V(CO)_6]^-$

in the presence of ligand have been reported [12,13]. The bis(diphenylphosphino)methane (DPPM) product has been detected by infrared spectroscopy during $[V(CO)_6]^-$-DPPM photolyses, but it readily undergoes photoconversion to *cis*-$[V(CO)_4DPPM]^-$ [12].

Similarly, when $[V(CO)_5NH_3]^-$ decomposes in the presence of isocyanides, good yields (65—80%) of $[V(CO)_5CNR]^-$ are obtained. For example, treatment of a liquid ammonia-acetonitrile solution of thermally unstable $[Et_4N]$-$[V(CO)_5NH_3]$ (9.8 mmol) (prepared, most conveniently, in situ — see later) with three equivalents of CH_3NC, provided after removal of solvent at —20 to 0°C and recrystallization from acetone-diethyl ether, a 68% yield (2.35 g) of bright yellow, analytically pure $[Et_4N][V(CO)_5CNCH_3]$. Alternatively, addition of solid magenta $[Ph_4As][V(CO)_5NH_3]$ [15] (1.7 mmol) to a tetrahydrofuran solution containing three equivalents of CH_3NC at 0°C gave within several minutes an orange-yellow solution of $[V(CO)_5CNCH_3]^-$, which was isolated in 83% yield (0.86 g) as the golden-red crystalline $[Ph_4As][V(CO)_5$-$CNCH_3]$. By identical methods orange $[Et_4N][V(CO)_5CNC_6H_5]$, yellow $[Et_4N][V(CO)_5CN\text{-t-Bu}]$ and yellow $[Et_4N][V(CO)_5CNC_6H_{11}]$ have been isolated as air sensitive crystalline materials. Infrared and ^1H NMR spectra (Table 1) and elemental analyses are entirely consistent with the proposed formulations.

TABLE 1

INFRARED AND ^1H NMR SPECTRA FOR $V(CO)_5L^-$

		ν(CN) (cm^{-1})	ν(CO) [a,g] (cm^{-1})	Chemical shift(ppm), Multiplicity *b*
I	$[Et_4N][V(CO)_5CH_2(PPh_2)_2]$	—	1965m, 1815s	3.18 t(2H), *J*(PH) = 4.3 Hz, 7.06—7.24m, 7.32—7.6m (20H) [c]
II	$[Et_4N][V(CO)_5((p\text{-}ClC_6H_4)_3P)]$	—	1970m, 1825s	7.3—7.6m (12H)
III	$[Et_4N][V(CO)_5CNCH_3]$	2120w	1965m, 1930s	— [d]
IV	$[Ph_4As][V(CO)_5CNCH_3]$	2120w	1970m, 1830s	3.18 broad s (3H) [e]
V	$[Et_4N][V(CO)_5CNt\text{-}Bu]$	2092w, 2062w	1955m, 1828s	1.39s (9H)
VI	$[Et_4N][V(CO)_5CNC_6H_{11}]$	2080w	1955m, 1825s	1.35—1.82m (11H) [f]
VII	$[Et_4N][V(CO)_5CNC_6H_5]$	2040w	1930m, 1845s	7.05—7.46m (5H)

[a] Solvent = CH_3CN except for V and VII (THF). [b] Solvent = CD_3CN; TMS reference; resonance positions of cations are not shown. [c] ^{31}P NMR (RF = 40.5 MHz on 100 MHz instrument); Solvent = CD_3CN; resonance positions relative to an external H_3PO_4 (85% in D_2O) standard at room temperature; positive shift value (broad resonance indicating coordinated PPh_2 group) is downfield of H_3PO_4; δ(ppm): +51(broad), —24.9 (doublet), *J*(PP) = 75.1 Hz. Similar ^{31}P NMR of $[V(CO)_5L]^-$ species have been reported previously [12]. [d] Methyl resonance position of CH_3NC is obscured by overlap of the methylene resonance signal of Et_4N^+. [e] Broadened signal (10 Hz at half-height) is undoubtedly caused by N and V, both quadrupolar nuclei. The methyl resonance in $C_5H_5V(CO)_3CH_3$ is similarly broadened (4 Hz at half-height) [16]. [f] Part of this broad multiplet overlaps the methyl resonance of Et_4N^+. [g] A weak shoulder at ca. 1860 cm^{-1} was also observed in most spectra. This may arise from trace amounts of $V(CO)_6^-$ in the products [17]. In the absence of L, $V(CO)_5NH_3^-$ decomposes to give greater than 50% yields $V(CO)_6^-$.

The amine group in $[V(CO)_5NH_3]^-$ is readily lost in solution above —20°C. This decomposition process may generate the same coordinately unsaturated $[V(CO)_5]^-$ which has been produced previously only by the photolysis of $V(CO)_6^-$ [9]. Our studies indicate that the use of $[V(CO)_5NH_3]^-$ will be an important route to new $[V(CO)_5L]^-$ whenever L and/or $[V(CO)_5L]^-$ are photosensitive. Further, in contrast to the photosubstitution reactions of $[V(CO)_6]^-$, there is no need to carefully monitor the course of these thermal reactions to minimize the presence of undesired materials (e.g., unreacted $[V(CO)_6]^-$ or $[V(CO)_4L_2]^-$). Rehder previously prepared $[V(CO)_5NH_3]^-$ in 55% yield by the photolysis of $[V(CO)_6]^-$ for long periods (ca 24 h) in liquid ammonia [8], followed by a 3 day Soxhlet extraction with ammonia to remove impurities. We have discovered a much quicker (2—3 h) and nearly quantitative route (85—95% yields) to $[V(CO)_5NH_3]^-$ by the acidification of $[V(CO)_5]^{3-}$ in liquid ammonia.* Attempts to extend these reactions to other metal carbonyl anions are in progress.

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*A liquid ammonia solution of $Na_3V(CO)_5$ was prepared from $[Na(diglyme)_2][V(CO)_6]$ (2.00 g, 3.92 mmol) and sodium metal (0.28 g, 12.2 mmol) as described previously (requires approx. 0.5 h) [14]. Solid ammonium chloride (0.63 g, 11.6 mmol) was added all at once to the stirred cold (—78°C) solution. The deep magenta solution was then refluxed for 0.5 h. Addition of a solution of tetraphenylarsonium chloride (2.61 g, 5.98 mmol) in ethanol (40 ml) caused an immediate precipitation of deep violet-red crystalline solid. After refluxing the solution for 0.5 h to ensure complete metathesis, the solid was removed by filtration, washed with cold (0°C) 6 *N* aqueous ammonia to remove NaCl, washed with cold (0°C) absolute ethanol and dried under vacuum at room temperature for 12 h. A nearly quantitative yield (2.20 g, 95%) of analytically pure $[Ph_4As][V(CO)_5NH_3]$ was thereby obtained. This material may be stored indefinitely under a nitrogen atmosphere at room temperature. (Nujol mull spectrum in ν(CO) region: 1958m, 1779vs, 1747vs cm^{-1}).