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THE CHEMISTRY OF METAL CARBONYL ANIONS

VII *. REDUCTION OF CYCLOPENTADIENYLMETAL CARBONYLS IN HEXAMETHYLPHOSPHORAMIDE

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Summary

The alkali metal reductions of a series of monomeric and dimeric cyclopentadienyl-substituted metal carbonyls in hexamethylphosphoramide provide principally $C_5H_5V(CO)_3^{2-}$ from $C_5H_5V(CO)_4$, $Mn(CO)_4^{3-}$ from $C_5H_5Mn(CO)_3$, $Co(CO)_4^-$ from $C_5H_5Co(CO)_2$, and $C_5H_5M(CO)_y^-$ from corresponding $[C_5H_5M(CO)_y]_2$, where M = Mo, Fe and Ni for y = 3, 2 and 1, respectively. The spectral and chemical properties of many of these reduced species are described.

Introduction

We have recently shown hexamethylphosphoramide (HMPA) to be a unique solvent for the generation of metal carbonyl anions, including the first non cluster metal carbonyl trianions [1]. Our previous observations that the compounds $M(CO)_6$ (M = Cr, Mo and W) [2] are cleanly converted to the corresponding dianions $M(CO)_5^{2-}$ by alkali metals in HMPA suggested that this procedure might also be a useful route to η^5-cyclopentadienyl-substituted metal carbonyl dianions, of which $C_5H_5V(CO)_3^{2-}$ is the only previously known example [3]. The results of this investigation will now be described.

Experimental

General procedures and materials

All operations were carried out under an atmosphere of purified nitrogen or argon further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate and molecular sieves. Solutions were transferred by stainless steel cannulae and syringes; otherwise reactions were performed by

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* For part VI see Ref. 33.

using standard Schlenk apparatus [4]. Reagent grade tetrahydrofuran was freshly distilled from the benzophenone ketyl of potassium under an argon atmosphere. Hexamethylphosphoramide (Aldrich) was distilled in vacuo from calcium hydride and subsequently from sufficient sodium to initially give a homogeneous blue solution under argon. Excessive sodium should not be used in the second step as it decomposes HMPA during the distillation giving dimethylamine and diamidophosphite ion [5]. Cyclopentadienyltetracarbonylvanadium was obtained by the method of Keblys and Dubeck [6], cyclopentadienyltricarbonylmanganese and cyclopentadienyldicarbonylcobalt were purchased (Strem Chemicals) and used without further purification. Cyclopentadienylmetal carbonyl dimers of molybdenum, iron and nickel were purchased (Alfa—Ventron), while $[C_5H_5W(CO)_3]_2$ was prepared according to a literature method [7]. Triphenylstannyl chloride (Alfa) and other reagents were obtained from commercial sources except where noted.

IR spectra were recorded on a Perkin—Elmer 237B Spectrometer. Solution spectra were obtained in sealed sodium chloride cells equipped with stainless steel Luer stopcocks to permit filling via syringe outside the glove box with essentially complete exclusion of air. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan, and Galbraith Laboratories.

Reduction of η^5-cyclopentadienyltetracarbonylvanadium and preparation of tetraethylammonium η^5-cyclopentadienyltricarbonyltriphenylstannylvanadate, $[Et_4N][Ph_3SnV(CO)_3C_5H_5]$

Clean sodium metal (0.10 g; 4.4 mmol) was added with stirring to a solution of $C_5H_5V(CO)_4$ (0.50 g; 2.2 mmol) in 25 ml of moisture- and dioxygen-free HMPA. After stirring for 3 h at room temperature the reduction was judged to be complete (other reductions monitored by infrared spectra showed the reaction to be complete within 1 h) and 1.80 g (4.7 mmol) of Ph_3SnCl was added by sidearm. (Infrared spectra at this time show ν(CO) at 1891s and 1795s (br) cm^{-1} after addition of either one or two equivalents of Ph_3SnCl.) Addition of a dioxygen-free aqueous solution of tetraethylammonium bromide (1.0 g; 4.8 mmol in 50 ml of H_2O) caused the precipitation of a yellow solid which was filtered (medium porosity fritted disc), dried in vacuo, washed with ether and dried again. The solid was taken up in acetone and filtered through a one-inch column of silica gel. Excess diethyl ether was then added to filtrate. As the ether/acetone mixture was evaporated, yellow crystals began to appear; addition of heptane caused additional crystals to fall from solution. These were washed with pentane and dried to give 0.40 g (26% yield) of analytically pure yellow $[Et_4N][Ph_3SnV(CO)_3C_5H_5]$ (m.p. with decomp. 130°C). Anal. Found: C, 60.07; H, 6.02; N, 1.98; Sn, 17.35. $C_{34}H_{40}NO_3SnV$ calcd.: C, 60.02; H, 5.94; N, 2.06; Sn, 17.44%.

Reduction of η^5-cyclopentadienyltricarbonylmanganese and preparation of tetraethylammonium bis(triphenylstannyl)tetracarbonylmanganate, $[Et_4N][(Ph_3Sn)_2Mn(CO)_4]$

A solution of $C_5H_5Mn(CO)_3$ (0.50 g, 2.45 mmol) in 20 ml of HMPA was treated with sodium (0.14 g, 6.1 mmol) until the deep blue color of excess sodium in HMPA persisted. Spectra indicated conversion of $C_5H_5Mn(CO)_3$ to $NaMn(CO)_5$ and finally $Na_3Mn(CO)_4$. Excess triphenylstannyl chloride (2.70 g, 7.0 mmol) in 10 ml of THF changed the blue color to a deep red. Addition of 1.30 g (6.2 mmol) of tetraethylammonium bromide in 200 ml of water gave a fine cream precipitate which was washed with water to remove excess Et_4NBr, dried in vacuo, washed with excess ethyl ether to remove unreacted Ph_3SnCl and dried. Recrystallization of the product from acetone/diethyl ether provided 1.58 g (64%) of analytically pure colorless $[Et_4N]$ [*cis*-$(Ph_3Sn)_2Mn(CO)_4$] (m.p. 205—209°C, dec.) Anal. Found: C, 57.55; H, 5.07; N, 1.45; Sn, 23.87. $C_{48}H_{50}O_4MnNSn_2$ calcd.: C, 57.81; H, 5.05; N, 1.40; Sn, 23.80%. The infrared spectrum of this species in THF in the carbonyl stretching region shows bands at 2000s, 1922(sh) and 1913vs cm^{-1}, which is consistent with a molecule of *cis* configuration [1].

Reduction of cyclopentadienylcarbonylmetal dimers in HMPA

These reductions were carried out as described above for the monomeric cyclopentadienylmetal carbonyls. No reduction products were isolated, however, their infrared spectra (for Mo and Fe, see Results and discussion) were superimposable with those of genuine monoanions [23]. The nickel reduction product is discussed later in the paper.

Results and discussion

Reduction of $C_5H_5V(CO)_4$ in HMPA

Cyclopentadienyltetracarbonylvanadium is reduced by sodium metal in HMPA principally to $C_5H_5V(CO)_3^{2-}$, the only known cyclopentadienyl-substituted metal carbonyl dianion [3]. A comparison of the infrared spectrum of the reduced species prepared in HMPA with those of genuine $Na_2C_5H_5V(CO)_3$ obtained by the reduction of $C_5H_5V(CO)_4$ in sodium in liquid ammonia [8] and sodium amalgam in THF [9] show that all three reduction processes give the same anionic product. Hexamethylphosphoramide solutions of $Na_2C_5H_5V(CO)_3$ in the presence of dissolved sodium metal show bands in the carbonyl stretching region at 1742s and 1619s cm^{-1} which we attribute to $C_5H_5V(CO)_3^{2-}$. This first reported solution spectrum of $C_5H_5V(CO)_3^{2-}$ compares well with the previously reported mull spectrum of $Cs_2[C_5H_5V(CO)_3]$ (ν(CO): 1748, 1645 cm^{-1}) [10] *. Weaker bands are also present at 1893 and 1778 cm^{-1} as well as a weak spike at 1573 cm^{-1}. The latter is undoubtedly due to a reduction product of HMPA since it has been observed in sodium reductions of numerous other organometallics as well as in solutions of sodium in HMPA. Exposure of the solution to air causes the sharp bands at 1893 and 1778 cm^{-1} to grow as the bands due to $C_5H_5V(CO)_3^{2-}$ decline in intensity. More extensive air oxidation causes the bands due to $C_5H_5V(CO)_3^{2-}$ to disappear completely. Bands remain at 1893s, 1778vs and a rather broad unsymmetrical band centered at ca. 1575 cm^{-1} (attributed to a reduction product of HMPA). We have found that the Na/Hg reduction product of $C_5H_5V(CO)_4$ in THF contains a much higher pro-

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* A similar spectrum of $[Me_4N]_2[C_5H_5V(CO)_3]$ (ν(CO): 1742, 1630 cm^{-1}) in acetonitrile was reported shortly after submission of this paper for publication [32].

portion of the "oxidized" species than reductions conducted in HMPA or liquid ammonia. This substance remains uncharacterized but may be $HV(CO)_3C_5H_5^-$ [12].

Chemical confirmation of the dianion formulation has also been obtained by preparing a triphenylstannyl derivative according to eq. 1:

$$C_5H_5V(CO)_3{}^{2-} + Ph_3SnCl \rightarrow Ph_3SnV(CO)_3C_5H_5{}^- + Cl^- \qquad (1)$$

Infrared monitoring of this reaction shows that $Ph_3SnV(CO)_3C_5H_5^-$ is formed almost quantitatively in HMPA, and the product appears to have little or no tendency to react with a second equivalent of Ph_3SnCl. Purification of the product by chromatography on silica gel and subsequent recrystallization provides only about a 26% yield of analytically pure substance. This compound is the first reported anionic derivative of $C_5H_5V(CO)_3{}^{2-}$, although the related $C_5H_5V(CO)_3CN^-$ (ν(CO) in diglyme: 1942s, 1842vs cm^{-1}) has been prepared by the reaction of $(C_5H_5)_2V_2(CO)_5$ with NaCN [9]. The triphenylstannyl derivative may be isolated as a slightly air-sensitive yellow crystalline tetraethylammonium salt (ν(CO) in HMPA: 1891s, 1795s (br) cm^{-1}), which dissolves in many polar organic solvents to yield extremely air sensitive solutions. Interestingly, its spectrum is quite similar to that resulting from the oxidation of $C_5H_5V(CO)_3{}^{2-}$ mentioned above. The only previously reported reaction of $C_5H_5V(CO)_3{}^{2-}$ is that with aqueous acid which yields $(C_5H_5)_2V_2(CO)_5$ [13].

Reduction of $C_5H_5Mn(CO)_3$ and $C_5H_5Co(CO)_2$ in HMPA

In contrast to the clean reduction of $C_5H_5V(CO)_4$ to the dianion, we find that the reduction of $C_5H_5Mn(CO)_3$ and $C_5H_5Co(CO)_2$ by sodium metal in HMPA do not yield cyclopentadienyl carbonyl dianions in significant amounts. Instead, rather ill-defined ligand redistribution reactions occur which provide principally $Co(CO)_4^-$ and $Mn(CO)_4{}^{3-}$. We have observed the same spectral changes for the reduction of $C_5H_5Co(CO)_2$ in HMPA as reported by Bergman and coworkers in a recent communication. They demonstrated that $Co(CO)_4^-$ and a novel binuclear radical anion, $[C_5H_5CoCO]_2^-$ are formed [14]. Surprisingly, the latter species does not reduce further to $[C_5H_5CoCO]_2{}^{2-}$ or $C_5H_5CoCO^{2-}$, which are formally analogous to $[Fe(CO)_4]_2{}^{2-}$ of $Fe(CO)_4{}^{2-}$, respectively. However, it is likely that the stability of highly reduced transition metal species is a sensitive function of the number of π-acceptor ligands attached to the metal center; i.e., if other factors are approximately the same (e.g., formal oxidation state of metal), the fewer the coordinated π-acceptor ligands the less stable a highly reduced transition metal species should be. This hypothesis is based on the Chatt—Dewar—Duncanson model for bonding in organotransition metal compounds [28] which qualitatively explains, e.g., why $Co(THF)_4^-$ should be less stable than $Co(CO)_4^-$, and also why $C_5H_5V(CO)_3{}^{2-}$ is likely to be more stable than $C_5H_5Mn(CO)_2{}^{2-}$ (vide infra) or $C_5H_5CoCO^{2-}$. It is possible that the pseudo-octahedral structure of $C_5H_5V(CO)_3{}^{2-}$ also enhances its relative stability, however.

Another interesting observation on the sodium reduction of $C_5H_5Co(CO)_2$ in HMPA is that $Co(CO)_4^-$ is stable towards reduction in the presence of excess sodium in HMPA at room temperature. In this respect, the behavior of $Co(CO)_4^-$ contrasts markedly with that of $Mn(CO)_5^-$ which is described below.

Reduction of $C_5H_5Mn(CO)_3$ by sodium in HMPA initially gives $Mn(CO)_5^-$ and small amounts of uncharacterized species. Bands due to $C_5H_5Mn(CO)_3$ (2017s, 1926s cm^{-1}) in HMPA become less intense as new absorptions form at 1896, 1865 and 1778 cm^{-1}. The 1896 cm^{-1} and part of the 1865 cm^{-1} bands have been shown to be due to $Mn(CO)_5^-$ by quenching the mixture at an intermediate stage in reduction to give bona fide $Ph_3SnMn(CO)_5$ [16]. It should also be noted that $C_5H_5Mn(CO)_3$ does not react with HMPA under these conditions. Reduction of $C_5H_5Mn(CO)_3$ by Na/Hg in diglyme is also reported to yield $Mn(CO)_5^-$ [17]. A preparation of $Mn_2(CO)_{10}$ from the relatively inexpensive $CH_3C_5H_4Mn(CO)_3$ is based on this reduction [18].

Further reduction with four or more equivalents of sodium provides a blue solution (due to dissolved sodium) which gives an infrared spectrum containing bands attributable to $Mn(CO)_4^{3-}$ (ca. 1670(br) cm^{-1}), an oxidation product of $Mn(CO)_4^{3-}$ (1722 cm^{-1}) [1], and a new uncharacterized species (1815m, 1781s cm^{-1}) which is not obtained by the reduction of $Mn(CO)_5^-$ in HMPA [1]. For comparison, the HMPA solution spectrum of $Mn(CO)_4^{3-}$ is shown in Fig. 1. We have experienced considerable difficulty in obtaining spectra of $Mn(CO)_4^{3-}$ free of oxidation product(s). The presence of a slight excess of sodium metal in the HMPA, however, minimizes this problem. Effectively, the blue color of Na in HMPA ensures the absence of dioxygen and moisture in solution. However, we find that $Mn(CO)_4^{3-}$ oxidation is not reversed significantly by adding excess sodium, thus good quality infrared cells and inert atmosphere are a must for obtaining reasonable spectra of $Mn(CO)_4^{3-}$. Although we have subsequently prepared $Mn(CO)_4^{3-}$ by reduction of $Mn(CO)_5^-$ in HMPA [1], the manganese

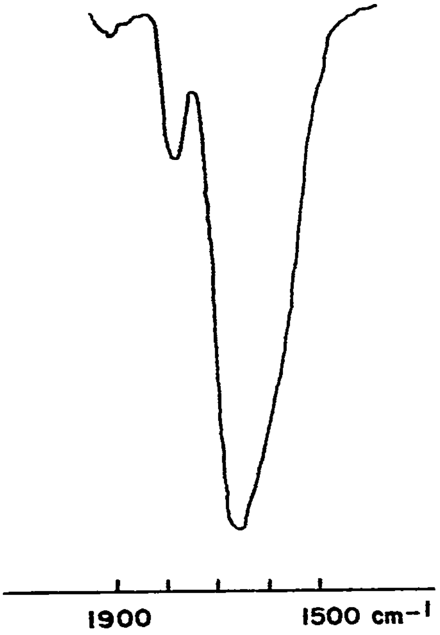

Fig. 1. Solvent compensated infrared spectrum of $Na_3Mn(CO)_4$ in the carbonyl stretching frequency region in HMPA. Positions of bands: 1805w, 1670vs cm^{-1}.

trianion was first prepared in this study. Attempts to isolate the species absorbing at 1865 and 1781 cm^{-1} from HMPA have not been successful.

Treatment of the blue solution with three equivalents of Ph_3SnCl gave a 64% yield of *cis*-$(Ph_3Sn)_2Mn(CO)_4^-$ which is derived from $Mn(CO)_4^{3-}$ and isolated as the tetraethylammonium salt. No evidence was obtained for the presence of other carbonyl-containing derivatives in the final product. Other reactions of $Mn(CO)_4^{3-}$ and the related $Re(CO)_4^{3-}$ will be described in due course [19].

Reduction of $[C_5H_5M(CO)_3]_2$ *(M = Mo),* $[C_5H_5Fe(CO)_2]_2$ *and* $[C_5H_5NiCO]_2$ *in HMPA*

In view of the fact that $M_2(CO)_{10}$ are reduced eventually via $M(CO)_5^-$, to metal carbonyl trianions [1], the reduction of $[C_5H_5M(CO)_y]_2$ in HMPA was examined with the hope of preparing corresponding $[C_5H_5M(CO)_{y-1}]^{3-}$ which would be anionic derivatives of $[C_5H_5M(CO)_{y-1}]_2$, known for M = Cr and Mo for $y - 1 = 2$ [20,21]. In the case of the Mo and Fe dimers, reduction did not proceed beyond the monoanion stage. Dissolution of $[C_5H_5Mo(CO)_3]_2$ (which absorbs in THF at 2013, 1957 and 1912 cm^{-1}) in HMPA gives bands at 2046m, 2009s, 1951s, 1901s and 1786s cm^{-1} for a 0.05 *M* solution. Undoubtedly, HMPA is causing disproportionation of $[C_5H_5Mo(CO)_3]_2$ according to eq. 2:

$$[C_5H_5Mo(CO)_3]_2 + HMPA \rightleftharpoons [C_5H_5Mo(CO)_3HMPA^+]\,[C_5H_5Mo(CO)_3^-] \qquad (2)$$

Significantly more base sensitive $[C_5H_5Cr(CO)_3]_2$ is reported to undergo heterolytic cleavage in dimethylformamide (DMF) (which does not disproportionate the molybdenum analog) to yield $C_5H_5Cr(CO)_3^-$ and $C_5H_5Cr(CO)_3DMF^+$. The latter absorbs at 2039, 1977 and 1952 cm^{-1} [22], in close agreement with the three high energy bands of $[C_5H_5Mo(CO)_3]_2$ in HMPA. Reduction of $[C_5H_5Mo(CO)_3]_2$ with an excess of sodium in HMPA provides a solution which absorbs at only 1902s and 1787s cm^{-1}, which is due to $C_5H_5Mo(CO)_3^-$. This spectrum is nearly identical to that of a THF solution of $[Ph_4As]\,[C_5H_5Mo(CO)_3]$ in the carbonyl stretching frequency region: 1898s, 1784s cm^{-1} [23].

In contrast, $[C_5H_5Fe(CO)_2]_2$, which is more resistant to disproportionation than $[C_5H_5Mo(CO)_3]_2$ [3], dissolves in HMPA with no cleavage as evidenced by its solution spectrum (ν(CO): 1988vs, 1944m, 1785vs cm^{-1}). Addition of excess sodium metal to this solution provides after 45 minutes two bands of approximately equal intensity which are due to $C_5H_5Fe(CO)_2^-$ (ν(CO): 1869s, 1797s cm^{-1}). Spectra of $[Ph_4As][C_5H_5Fe(CO)_2]$ in THF-acetonitrile (ν(CO): 1867s, 1792s cm^{-1}) are essentially identical [23].

It is appropriate to note here that the infrared spectra of alkali metal salts of carbonyl monoanions in HMPA are generally not complicated by ion pair effects such as those which occur in THF [23,24] since the cation is strongly solvated [5]. Consequently, carbonyl monoanions and most other bases (the electron is exceptional in this regard [25]) which interact only weakly with HMPA exist in an essentially symmetrical "solvent surrounded" environment [24] and provide solution spectra independent of cation. A particularly interesting observation in this regard is that benzylmagnesium chloride gives a deep red solution in HMPA due to full ionization, while in THF it provides colorless solutions due to incomplete cleavage of the benzyl—magnesium bond [5]. However, we have obtained infrared evidence that more highly charged anions such as $M(CO)_4{}^{2-}$ (M = Fe, Ru and Os) [26] and $M(CO)_4{}^{3-}$ (M = Mn and Re) [1, 19] participate in ion pairing to some extent in HMPA.

Bis(carbonylcyclopentadienylnickel) is only slightly soluble in HMPA, giving a red solution which has ν(CO) bands at 1944m, 1890w and 1846s cm^{-1}, compared to a corresponding solution spectrum in THF which shows only two bands (ν(CO): 1890m and 1848s cm^{-1}). Dilution of the HMPA solution by THF causes the 1944 cm^{-1} band to disappear. This observation suggests that some heterolysis of the dimer occurs in neat HMPA since the process is reversed by diluting HMPA with unreactive THF. On addition of sodium metal to the dimer in HMPA, all dimer dissolves to give a deep brown-yellow solution which has an intense sharp band at 1854 cm^{-1} which we attribute to $C_5H_5NiCO^-$. Although this anion has been considered to be produced by potassium [27] or electrochemical reduction [29] of $[C_5H_5NiCO]_2$, no infrared spectrum of this substance has been previously reported. Unfortunately, attempts to prepare stable derivatives from this substance in HMPA failed. For example, addition of an equivalent of Ph_3SnCl to the "anion" in HMPA caused complete disappearance of the 1854 cm^{-1} band and formation of a single sharp band at 2005 cm^{-1}, possibly due to $C_5H_5Ni(CO)SnPh_3$. However, this deep red product rapidly decays at room temperature to green black $(C_5H_5Ni)_3(CO)_2$ [30] (ν(CO) in HMPA: 1755 cm^{-1}). A related orange-red derivative, $C_5H_5Ni(CO)SnMe_3$, prepared by heating $[C_5H_5NiCO]_2$ with hexamethylditin, absorbs at 1999 cm^{-1} [31]. But, attempts to prepare this material from the "anion" and Me_3SnCl resulted in the immediate formation of $[C_5H_5NiCO]_2$ and $(C_5H_5Ni)_3(CO)_2$.

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