31.1; Ni(III), 7.65 (iodometric determination).

Method 2. A solution of [Ni(VPP)Br_2] (2.0 g, 3.3 mmol) in the minimum amount of chloroform was treated with bromine in chloroform (20 mL, ~5% v/v). On standing for a few hours, black crystals separated; these were filtered off, rinsed with diethyl ether (5 mL), and dried in vacuo (1.9 g, 64%). Anal. Calcd for [Ni(VPP)Br_3]: C, 44.9; H, 3.2; Br, 34.55. Found: C, 44.8; H, 3.1; Br, 34.5.

Results and Discussion

Treatment of the orange diamagnetic [Ni(VPP)Br_2] with bromine in chloroform or benzene yields the brown–black [Ni(VPP)Br_3], obtained as a monosolvate from the latter solvent. The complex is unstable in solution but behaves as a nonelectrolyte in freshly prepared 10^{-3} M 1,2-dichloroethane or nitromethane. The magnetic susceptibility ($\mu_{\mathrm{eff}} = 1.98\ \mu_B$) is consistent with the presence of low-spin d^7 nickel(III).[2] The far-IR spectrum contains three absorbtions attributable to ν(Ni–Br) at 276, 265, and 220 cm^{-1} [10] and is consistent with a five-coordinate complex. The electronic spectrum in dichloromethane exhibits absorptions at 0.81 (ϵ 22), 1.43 (ϵ 138), 2.10 (ϵ 2820), 2.69 (ϵ 2190), and 3.41 (ϵ 13 200) μm^{-1}, and the solid reflectance spectrum is essentially similar, exhibiting bands at 0.83, 1.35, 2.10, and 2.50 μm^{-1}. The spectrum is again consistent with a five-coordinate monomer but does not distinguish between a trigonal-bipyramidal (C_{2v}) or a square-pyramidal (C_s) structure since four spin-allowed transitions are expected for either structure.

The EPR spectrum of powdered [Ni(VPP)Br_3] at −150 °C consists of a single broad absorbtion ($g = 2.06$). In dichloromethane solution at room temperature the spectrum shows a quartet ($g = 2.16$, $A_{\mathrm{iso}} = \sim 65$ G) due to coupling to a single bromine atom (^{79}Br, ^{81}Br, $I = {}^3/_2$), upon which further fine structure in the form of a 1:2:1 triplet is evident, consistent with two equivalent phosphorus atoms (^{31}P, $I = {}^1/_2 A_{\mathrm{iso}} = \sim 9$ G). These data are consistent with a C_{2v} structure (I) in which the unpaired electron shows resolvable coupling only to the P_2Br donors in the equatorial plane. The alternative square-pyramidal (C_s) structure would be expected to show coupling to two equivalent bromines and two phosphorus atoms in the basal plane.

A sample of [Ni(VPP)Br_3] evolved bromine on strong heating (>300 °C), and [Ni(VPP)Br_2], identified by analysis and its electronic spectrum[7] remained. The solid also decomposed slowly in an open vessel at room temperature. The decomposition could be monitored by observing the decrease in μ_{eff} from 1.98 to ~0.2 μ_B (corresponding to the measured susceptibility of [Ni(VPP)Br_2] and probably attributable to temperature-independent paramagnetism). The rate of decomposition varied with the state of subdivision of the sample, being fastest for very thin films of the solid and slowest for the bulk solid; the average time to revert completely to [Ni(VPP)Br_2] is about 2 months. A sample kept in a sealed tube showed very little decomposition in this time. This suggests that [Ni(VPP)Br_3] slowly evolves bromine, the reaction proceeding to completion only when the bromine can escape, but if the bromine is not removed, decomposition is minimal. Certainly, powdered [Ni(VPP)Br_2] rapidly turns to black [Ni(VPP)Br_3] when exposed to bromine vapor. A careful examination (analysis and IR and electronic spectra) of the "[Ni(VPP)Br_2]" produced by this decomposition showed it to be identical with a genuine sample.[7] Neither the phosphorus nor the unsaturated backbone of the ligand are attacked by the evolved bromine under these conditions.[11]

The stability of nickel(III) complexes of this type is very sensitive to changes in the ligand. The tetrahedral [Ni(tVPP)Br_2]$_n$[12] (tVPP = *trans*-1,2-bis(diphenylphosphino)ethylene) is not oxidized by bromine, while for [Ni(VPP)$_2$Br]BPh_4 [7] or [Ni(VAA)Br_2][13] (VAA = *cis*-1,2-bis(diphenylarsino)ethylene) oxidation to nickel(III) does occur, but the products are unstable, decomposing in a few hours.

Registry No. Ni(VPP)Br_3, 64771-39-7; Ni(VPP)Br_2, 23467-50-7.

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Bis(dimethylamido)tetrakis(*N*,*N*-dimethylcarbamato)dimolybdenum

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Received July 8, 1977

We report our preparation and characterization of the title compound, $Mo_2(NMe_2)_2(O_2CNMe_2)_4$, I, formed in the reaction between $Mo_2(NMe_2)_6$ and carbon dioxide.

Alkane solutions of $Mo_2(NMe_2)_6$[1] react rapidly with CO_2 (>6 equiv) at room temperature to give I as a pale yellow microcrystalline precipitate. When I is dissolved in benzene or toluene and reacted with a further excess of CO_2, the solution turns gray; we have been unable to isolate any pure compound from these solutions. When the reaction I + CO_2 (>2 equiv) is carried out in an NMR tube and followed by ^1H NMR spectroscopy, all proton resonances disappear with time.

These observations show a marked difference in the reactivity of $Mo_2(NMe_2)_6$ compared with $W_2(NMe_2)_6$.[2] The latter compound reacts[3] with CO_2 (≥6 equiv) to give $W_2(O_2CNMe_2)_6$ which has been structurally characterized.[4,5]

I is a pale yellow, air-sensitive, diamagnetic compound; it is appreciably soluble in toluene and benzene but only very sparingly soluble in alkane solvents. It is this fact which accounts for its ready isolation from the reaction between alkane solutions of $Mo_2(NMe_2)_6$ and CO_2. Attempts to recrystallize I were thwarted because I slowly decomposed in solution. The stability of I in this regard is comparable to that of $W(NMe_2)_3(O_2CNMe_2)_3$.[3,6]

In the mass spectrometer I shows a strong molecular ion $Mo_2(NMe_2)_2(O_2CNMe_2)_4^+$ (m/e 632) together with many other Mo_2-containing ions. The most intense ion (base peak) occurred at m/e 544. A comparison of the mass spectra obtained from protio $Mo_2(NMe_2)_2L_4$ and the labeled compounds $Mo_2(NMe_2)_2L_{4-x}L'_x$, where L = $O_2CN(CH_3)_2$, L′ = $O_2CN(CD_3)_2$, and $x = 1$–4, indicates that the base peak corresponds to $Mo_2(O_2CNMe_2)_4^+$.

The IR spectrum showed a strong broad band at 1578 cm^{-1}, typical of $\nu(NCO_2)$ in a bidentate carbamate ligand.[3] Full IR data are recorded in the Experimental Section.

Proposed Structure of $Mo_2(NMe_2)_2(O_2CNMe_2)_4$

We believe that $Mo_2(NMe_2)_2(O_2CNMe_2)_4$ adopts a structure akin to that found[4,5] for $W_2Me_2(O_2CNEt_2)_4$ and that the central $Mo_2N_2(O_2C)_4$ moiety may be represented by

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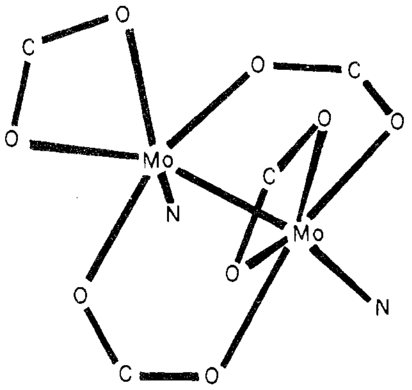

Figure 1. Proposed structure for the $Mo_2N_2(O_2C)_4$ core of the $Mo_2(NMe_2)_2(O_2CNMe_2)_4$ molecule. The $Mo_2N_2(O_2C)_4$ skeleton has C_{2v} symmetry.

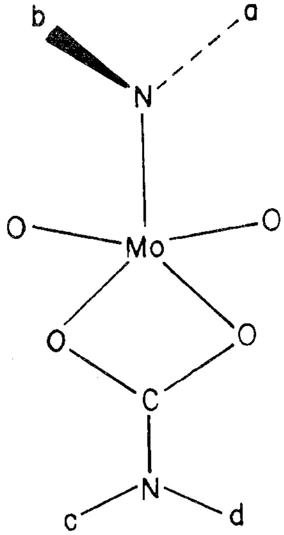

Figure 2. Proposed terminal view of $Mo_2(NMe_2)_2(O_2CNMe_2)_4$ showing the proximal (a) and distal (b) methyl groups. The Mo–NC_2 plane is not contained in the N–Mo–Mo–N plane and hence the carbamato methyls (c and d) of the terminally bonded ligand are inequivalent.

Figure 1. There are two bridging carbamato ligands, two terminally bonded carbamato ligands, and a planar N–Mo–Mo–N moiety. The central $Mo_2N_2(O_2C)_4$ moiety has virtual C_{2v} symmetry. The six nonhydrogen atoms of the carbamate ligand are planar and the coordination about the nitrogen atoms of the $MoNMe_2$ group is trigonal. (These presumptions are in keeping with all known structures of transition-metal dialkylamides[7] and *N,N*-dialkylcarbamates.[3,8]) The Mo–NC_2 moieties are arranged so that there are proximal and distal methyl groups with respect to the metal–metal triple bond. Since the N–Mo–Mo–N moiety is planar, it seems likely (for steric reasons) that the NC_2 planes will not be coplanar with the N–Mo–Mo–N plane but rather C_2 symmetry will pertain for the $Mo_2(NC_2)_2(O_2CNC_2)_4$ moiety. Thus in the ground state we predict there will be six types of methyl groups, a, b, c, d, e, and f, as shown in Figures 2 and 3. The ^{1}H NMR spectra recorded at various temperatures are consistent with these expectations.

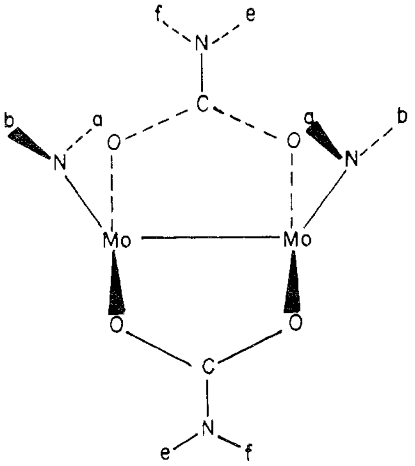

Figure 3. Proposed structure of $Mo_2(NMe_2)_2(O_2CNMe_2)_4$ viewed perpendicular to the Mo–Mo axis showing how the methyl groups are related by C_2 symmetry. The terminally bonded O_2CNMe_2 ligands are omitted for clarity.

^{1}H NMR Studies

Variable-temperature (+90 to −90 °C) ^{1}H NMR spectra were obtained for I in toluene-d_8 at 60, 100, and 270 MHz. At −60 °C and 270 MHz a low-temperature limiting spectrum was attained. This consisted of six resonances of equal integral intensity at δ = 5.01, 3.32, 2.93, 2.75, 2.72, and 2.46 (δ in ppm relative to Me_4Si) hereafter assigned to a, b, c, d, e, and f methyl groups, respectively. The assignment of a and b resonances to the $MoNMe_2$ groups is justified by a comparison of the ^{1}H NMR spectrum obtained for I with those for the deuterated compounds $Mo_2(NMe_2)_2L_{4-x}L'_x$, where L = $O_2CN(CH_3)_2$, L′ = $O_2CN(CD_3)_2$, and x = 1–4; the assignment of proximal and distal methyl groups to a and b resonances, respectively, follows from the arguments previously presented[1] for $Mo_2(NMe_2)_6$. A clear assignment of the resonances c, d, e, and f is not possible, but by analogy with the dynamical solution behavior of $W_2(O_2CNMe_2)_6$ we assign the resonances c and d to the terminally bonded bidentate carbamate ligand and the resonances e and f to the bridging carbamato methyl groups.[5]

At −50 °C (270 MHz) five resonances are observed at δ = 4.99, 3.30, 2.92, 2.75 (having twice the intensity), and 2.50 ppm. This we ascribe to a chemical shift change with temperature which now leads to the accidental degeneracy of the resonances d and e. At −40 °C five resonances are also observed, but, significantly, resonance c at δ = 2.93 ppm is broadened. This we ascribe to an exchange between the c and d methyl groups of the terminally bonded carbamate ligand (see Figure 2). At −20 °C, resonances a and b and e and f remain unchanged while c and d are approaching coalescence. At 0 °C, c and d have coalesced to a broad singlet while a, b, e, and f remain sharp. At +20 °C five sharp resonances are observed corresponding to the a, b, c = d, e, and f methyl groups.

Above 50 °C decomposition of the sample becomes rapid. In order to investigate the dynamical solution behavior of I above this temperature, freshly prepared samples of I in toluene-d_8 were inserted into the preheated probe of a 100-MHz spectrometer. At 80 °C three resonances were observed at δ = 4.95, 3.21, and 2.80 ppm in the integral ratio 1:1:4, respectively. Thus, at this temperature, exchange of all carbamato methyl groups (c, d, e, f) is rapid on the NMR time scale. This finding has a direct parallel in the observed ^{1}H NMR spectrum of $W_2(O_2CNMe_2)_6$ which at +70 °C shows a singlet, indicating rapid exchange of terminally bonded and bridging carbamato ligands.[3,5] Significantly for I, we do not observe rapid proximal (a) and distal (b) methyl-group exchange even at +80 °C. Above this temperature decomposition is too rapid to allow meaningful interpretation of the observed spectra.

We conclude that the ^{1}H NMR spectra of I are entirely consistent with the adoption of a structure akin to that found for $W_2Me_2(O_2CNEt_2)_4$, given that the $Mo_2(NC_2)_2$ moiety adopts the skew proximal–distal methyl orientation thus rendering the pairwise equivalence of the methyl groups as demanded by C_2 symmetry (see Figures 2 and 3).

Experimental Section

General Procedures. $Mo_2(NMe_2)_6$ was prepared as previously described.[1] ^1H NMR spectra (100 MHz) were obtained from a Varian XL-100 spectrometer equipped with a variable-temperature probe. ^1H NMR spectra (270 MHz) were obtained with the courtesy of the Department of Chemistry, Yale University. ^1H chemical shifts are reported as ppm downfield from Me_4Si. Temperatures were calibrated with methanol or ethylene glycol.

Infrared spectra were obtained from Nujol mulls between CsI plates using a Perkin-Elmer IR 283 spectrophotometer.

Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, using drybox sampling techniques. Mass spectra were obtained on an AEI MS9 by direct insertion with probe temperatures of 100–120 °C.

All preparations and other operations were carried out under a dry and oxygen-free nitrogen atmosphere or in vacuo, using standard Schlenk-type techniques. Samples were stored and handled in a Vacuum Atmospheres Dri Lab system.

Preparation of Bis(dimethylamido)tetrakis(*N*,*N*-dimethylcarbamato)dimolybdenum, $Mo_2(NMe_2)_2(O_2CNMe_2)_4$. $Mo_2(NMe_2)_6$ (1.66 mmol) was dissolved in hexane (30 mL). CO_2 (10.0 mmol, 6 equiv) was condensed into the reaction flask at liquid-nitrogen temperature. Upon warming to room temperature, a yellow solid precipitated out of solution. The reaction mixture was stirred for an additional 30 min and a yellow solid, $Mo_2(NMe_2)_2(O_2CNMe_2)_4$ (500 mg), was collected by filtration. Anal. Calcd for $Mo_2(NMe_2)_2(O_2CNMe_2)_4$: C, 30.39; H, 5.74; N, 13.29. Found: C, 30.57; H, 5.83; N, 13.01. $Mo_2(NMe_2)_2(O_2CNMe_2)_4$ is soluble in toluene; however, decomposition occurs over a period of 1–2 days.

Infrared data (Nujol mull between CsI plates): 360 (w, br), 396 (m), 449 (s), 568 (m), 610 (w), 641 (m), 645 (sh), 663 (s), 675 (m), 776 (m), 784 (m), 792 (m), 841 (w), 953 (s), 1039 (m), 1061 (vw), 1150 (vw), 1171 (vw), 1238 (s), 1262 (s), 1409 (vs), 1578 (vs) cm^{-1}.

A parent ion at *m/e* 632 in the mass spectrum corresponds to $Mo_2(NMe_2)_2(O_2CNMe_2)_4^+$ (based on ^{96}Mo).

Reaction of alkane solutions of $Mo_2(NMe_2)_6$ with $^{13}CO_2$ yielded the ^{13}C-labeled compound. ^1H NMR spectra identified the peaks at $\delta = 5.01$ and 3.32 ppm (relative to Me_4Si) as assignable to $MoNMe_2$ due to the absence of ^{13}C coupling; for $O_2{}^{13}CNMe_2$ ligands, $^3J_{^{13}C-H} = 3$ Hz.

Reaction of $Mo_2(NMe_2)_6$ with CO_2 in the Presence of $HN(CD_3)_2$. $Mo_2(NMe_2)_6$ (1.47 mmol) was dissolved in hexane (25 mL). CO_2 (6.0 mmol) and $HN(CD_3)_2$ (6.0 mmol) were condensed into the reaction flask at liquid-nitrogen temperature. Upon warming to room temperature, a yellow solid precipitated out of solution and was collected by filtration. IR and mass spectral data indicate the formation of the species $Mo_2(NMe_2)_2(O_2CN(CH_3)_2)_{4-x}(O_2CN(CD_3)_2)_x$. Exchange of free amine with $Mo-NMe_2$ groups was not observed.[2]

Infrared data (Nujol mull between CsI plates): 268 (m), 362 (m), 398 (m), 451 (s), 572 (m), 586 (w), 623 (m), 646 (s), 661 (s), 673 (s), 778 (s), 786 (s), 794 (s), 842 (m), 892 (w), 948 (s), 956 (s), 1040 (m), 1063 (m), 1097 (s), 1150 (m), 1163 (m), 1236 (s), 1262 (s), 1395 (m), 1408 (s), 1532 (s), 1576 (vs), 2070 (m), 2203 (m) cm^{-1}.

A parent ion pattern at *m/e* 640 in the mass spectrum was consistent with the formation of $Mo_2(NMe_2)_2(O_2CN(CH_3)_2)_{4-x}(O_2CN(CD_3)_2)_x$, where $x = 2$.

^1H NMR spectra (−60 °C) indicated the ratio of dimethylamido groups ($\delta = 5.01$, 3.32 ppm relative to Me_4Si) to dimethylcarbamato groups ($\delta = 2.92$, 2.74, 2.46 ppm relative to Me_4Si) was 2:2; cf. the 2:4 ratio in the protio complex.

Acknowledgment. We thank the Research Corp., the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. MPS-73-05016) for support of this work.

Registry No. I, 64728-46-7; $Mo_2(NMe_2)_2(O_2CN(CH_3)_2)_2(O_2CN(CD_3)_2)_2$, 64825-43-0; $Mo_2(NMe_2)_6$ (salt form), 33851-48-8; $Mo_2(NMe_2)_6$ (complex form), 51956-20-8; $HN(CD_3)_2$, 14802-36-9; CO_2, 124-38-9.

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Cationic Hydrido Complexes of Cobalt(III) with Diphenylphosphine

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Received August 3, 1977

Studies on the hydrido complexes of cobalt containing phosphorus ligands are of considerable current interest in homogeneous catalytic reactions. We have recently briefly reported[1] that hydrido derivatives of the type *cis*-$[CoH_2(P)_4]^+$ (P = tertiary or secondary phosphines) can be easily obtained by treatment at ambient conditions of alcoholic solutions of the phosphines and cobalt(II) salts of weakly coordinating anions with dihydrogen. The success of this synthetic procedure is very sensitive to changes in the phosphine ligands, and by this route we were able to prepare the *cis*-dihydrido complexes only with dimethylphenyl-, trimethyl-, and diphenylphosphine.

With the aim of elucidating the mechanism and the stoichiometry of the formation of the *cis*-$[CoH_2(P)_4]^+$ complexes, we have examined in some detail the reactions of diphenylphosphine with cobalt(II) salts of the type CoY_2 and "CoXY", where Y are weakly coordinating anions (ClO_4^-, BF_4^-) and X are halides or pseudohalides (Br^-, I^-, NCS^-, CN^-). In the course of the investigation we obtained a new series of hydrido complexes of the type *trans*-$[CoHX(HPPh_2)_4]Y$ and also the unusual cobalt(II) complexes $[Co(PPh_2)(HPPh_2)_3]Y$. Previously, it was reported[2] that diphenylphosphine reacts with methanolic solutions of cobalt bromide to give three different compounds: the five-coordinate $CoBr_2(HPPh_2)_3$, the tetrahedral $[CoBr(HPPh_2)_3]Br$, and a yellow diamagnetic $[CoBr(HPPh_2)_4]_2Br_2$. Our results show that this last compound should be reformulated as the hydrido derivative $[CoHBr(HPPh_2)_4]Br$.

This paper is part of a broad chemical study on the properties of transition-metal complexes with secondary phosphines.[3]

Experimental Section

Syntheses and handling of the complexes were carried out in the absence of air. The published procedure[4] was used to prepare diphenylphosphine. $CoY_2{\cdot}H_2O$ (Y = ClO_4, BF_4) were prepared from cobalt carbonate and aqueous HY. Microanalyses were performed by Mr. L. Turiaco, Istituto di Chimica Analitica, University of Padua. IR and visible spectra were recorded on a Perkin-Elmer 457 and on an Optica CF4R instrument, respectively. IR spectra of all described complexes show weak bands in the 2300–2360-cm^{-1} region, attributable to P–H stretching of the coordinated phosphines. Conductivity data were determined using an LKB conductance bridge. Magnetic susceptibilities were measured by the standard Gouy method and NMR spectra were taken using a Bruker 90-MHz spectrometer.

***cis*-$[CoH_2(HPPh_2)_4]ClO_4$.** (a) $HPPh_2$ (1.9 g, 10 mmol) was added to a solution of $Co(ClO_4)_2{\cdot}6H_2O$ (0.7 g, 2 mmol) in isopropyl alcohol (30 mL). The mixture was stirred for 48 h under an atmosphere of