drogen. A more gradual fragmentation of $[Rh_{15}(CO)_{27}]^{3-}$ cluster occurred under milder conditions (11 atm of an equimolar mixture of carbon monoxide and hydrogen, 150 °C, *N*-methylmorpholine, Rh:N = ca 5.0, cesium salt, 18-crown-6) as suggested by the sequential changes of the infrared spectra at reaction conditions. The relatively low solubility of $[Rh_{14}(CO)_{25}]^{4-}$ in 18-crown-6, the suggested assignments of the infrared spectra, and the slow precipitation of a material with a Rh:Cs atomic ratio of 3.6 may indicate the formation and precipitation of $[Rh_{14}(CO)_{25}]^{4-}$ (eq 3). These changes

$$\underset{1995,\ 1840\ cm^{-1}}{[Rh_{15}(CO)_{27}]^{3-}} \xrightarrow[CO]{H_2} \underset{1990,\ 1830\ cm^{-1}}{[Rh_{14}(CO)_{25}H]^{3-}} \xrightarrow[-H^+]{} \underset{1960,\ 1810\ cm^{-1}}{[Rh_{14}(CO)_{25}]^{4-}} \quad (3)$$

are attributed to the reaction of $[Rh_{15}(CO)_{27}]^{3-}$ with hydrogen and to the deprotonation by the amine of the resulting species by analogy with the Brønsted acid–base reactions of hydrido carbonyl clusters.[5,7] This proposal is also partially supported by the selective formation of $[Rh_{14}(CO)_{26}]^{2-}$ in the reaction of $[Rh_{15}(CO)_{27}]^{3-}$ with a protonic acid of a weakly electron-donating anion such as trifluoromethanesulfonic acid[23] (eq 4).

$$[Rh_{15}(CO)_{27}]^{3-} + H^+ \xrightarrow[CF_3SO_3H]{PPN^+\ salt} [Rh_{14}(CO)_{26}]^{2-} \quad (4)$$

Our attempts to study the solution structure of the cluster by ^{13}C and ^{13}C–^{103}Rh NMR[24] were precluded by the complexity of the spectra and the fluxionality of some of these ligands even at −90 °C (Figure 2). The most mobile set of carbonyls (unresolved broad multiplets: 226.2, 213.1, and 187.5 ppm) gives rise to a coalescence band (216.3 ppm) at −20 °C. On the other hand, the rigid set of ligands (edge bridges, symmetric (238.1 ppm, triplet) and asymmetric (219.7, doublet of doublets); terminals (180.1 ppm, doublet and 182.6 ppm, doublet) gives another coalescence band, (210.3 ppm) at a lower temperature of −60 °C. The terminal carbonyls responsible for the doublet at 182.6 ppm do not participate in either scrambling process even at 100 °C. The presence of three independent sets of carbonyls at temperatures higher than −20 °C was confirmed by the observation of characteristic rhodium decoupling frequencies shown in parenthesis for the coalescence bands at 216.3 (3.159 765 and 3.163 425 MHz), 210.3 (3.161 327 and 3.159 470 MHz), and 182.6 ppm (3.162 084 MHz) during ^{13}C–^{103}Rh NMR studies. The detachment of a "$Rh(CO)_2^+$" moiety from $[Rh_{15}(CO)_{27}]^{3-}$ may be related to the inability of the terminal carbonyl ligands represented by the resonance at 182.6 ppm to scramble with the other carbonyls.

This work has resulted in the convenient preparation of $[Rh_{15}(CO)_{27}]^{3-}$, and it suggests the importance of ion pairing in determining the reactivity of this cluster. This observation may be technologically relevant because ion pairing has been proposed to affect the behavior of homogeneous catalyst systems based in polynuclear rhodium complexes[25] which convert carbon monoxide and hydrogen into chemicals.[12]

Acknowledgment. The permission for the publication of this work by the management of Union Carbide Corp. is appreciated. The efforts of Mr. R. W. Dykstra in getting the ^{13}C–^{103}Rh NMR spectra are also appreciated.

Registry No. $[Cs(C_{12}H_{24}O_6)_2][Cs_2(C_{12}H_{24}O_6)_3][Rh_{15}(CO)_{27}]$, 79482-76-1; $[(Ph_3P)_2N]_3[Rh_{15}(CO)_{27}]$, 75506-17-1; $Rh(CO)_2(acac)$, 14874-82-9; CO, 630-08-0; H_2, 1333-74-0.

(23) J. L. Vidal and R. C. Schoening, *J. Organomet. Chem.*, in press.

(24) Professor Brian T. Heaton, University of Kent at Canterbury, England, informed us after this paper was written that he was also studying the solution structure of this cluster using similar techniques.

(25) L. Kaplan, U.S. Patents 3 944 588 (1976), 4 162 261 (1979), 4 224 237 (1980), and 4 197 253 (1980), German Patent 2643971 (1977), and Belgium Patent 867459 (1978).

(26) "The Synthesis and Characterization of Inorganic Compounds", William L. Jolly, Ed., Prentice-Hall, Englewood Cliffs, NJ, 1970, pp 100–102.

(27) G. Chaputt, G. Jeminet, and J. Julliard, *Can. J. Chem.*, **53**, 2240 (1975).

Contribution from the Istituto di Chimica Generale ed
Inorganica, 70126 Bari, Italy

A Study of the System $[Rh(C_2H_4)_2Cl]_2$–$P[N(CH_3)_2]_3$ and Evidence of *N,N,N',N'*-Tetramethylethylenediamine Formation via Intramolecular $N(CH_3)_2$ Transfer to η^2-C_2H_4. Reaction with CO_2 of the Rhodium Complexes

M. Aresta,* M. De Fazio, and P. Bruno

Received February 25, 1981

Among the trivalent phosphorus derivatives with the phosphorus bonded to nitrogen, the ligand tris(dimethylamino)phosphine has received considerable attention[1–3] owing to some attractive properties, e.g., steric hindrance and peculiar ^1H NMR spectrum. Indeed, the former can influence the geometry of metal complexes, and the latter can result in a useful tool for the identification of different complexes in mixtures.[4]

As an extension of our studies on transition-metal–CO_2 complexes stabilized by phosphorus ligands[5–8] we have prepared complexes of Rh(I) with the ligand $P(NMe_2)_3$ and studied properties and the reaction with CO_2.

Experimental Section

Reactions were carried out in an atmosphere of purified N_2 or CO_2 by vacuum-line techniques. Solvents were dried as reported in the literature and stored under nitrogen. Infrared spectra were run with a Perkin-Elmer 557 spectrophometer and ^1H NMR spectra with a Varian EM 360 A apparatus. Gas chromatographic analyses were performed with a Hewlett-Packard 5750 instrument, and molecular weights were determined cryoscopically in benzene as previously reported.[9] Reference *N,N,N',N'*-tetramethylhydrazine and *N,N,-N',N'*-tetramethylethylenediamine were purchased from Aldrich. CO_2 (99.99% pure) was from Matheson. ^1H NMR resonances are given as δ from internal Me_4Si. Coupling constants are given in hertz.

Preparation of the Complexes. Preparation of $RhCl(C_2H_4)[P(NMe_2)_3]_2$. To a filtered solution of $[RhCl(C_2H_4)_2]_2$ (0.224 g, 0.576 mmol) in toluene (20 mL) was added $P(NMe_2)_3$ (0.364 g, 2.23 mmol) and the solution stirred for 1 h at room temperature under nitrogen and then cooled to 0 °C. Toluene was evaporated in vacuo to half of the original volume and pentane added (10 mL). When the mixture was allowed to stand, at −20 °C, orange crystals deposited, mixed with a finely powdered yellow compound. When the solvent, was

(1) R. B. King, *Inorg. Chem.*, **2**, 936 (1963); R. B. King, and T. F. Kormowski, *ibid.*, **10**, 1188 (1971).

(2) P. Kalck and R. Poilblanc, *Inorg. Chem.*, **14**, 2779 (1975); J. J. Bonnet, Y. Jeannin, P. Kalck, A. Maisonnat, and R. Poilblanc, *ibid.*, **14**, 743 (1975) and reference therein.

(3) B. Denise and G. Pannetier, *J. Organomet. Chem.*, **161**, 171 (1978).

(4) F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Am. Chem. Soc.*, **92**, 1916 (1970).

(5) M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, and M. Manassero, *J. Chem. Soc., Chem. Commun.*, 636 (1975).

(6) M. Aresta and C. F. Nobile, *J. Chem. Soc., Dalton Trans.*, 708 (1977).

(7) M. Aresta and C. F. Nobile, *Inorg. Chim. Acta*, **24**, L49 (1977).

(8) P. Albano, M. Aresta, and M. Manassero, *Inorg. Chem.*, **19**, 1069 (1980).

(9) M. Aresta, C. F. Nobile, and A. Sacco, *Inorg. Chim. Acta*, **12**, 167 (1975).

(10) P. S. Brookes and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1079 (1967).

0020-1669/82/1321-0441$01.25/0

swirled, the yellow compound went in suspension while the orange crystals remained adherent to the wall of the flask. Pouring the suspension on a filter allowed the separation of the yellow compound from the orange crystals, which were then collected on a clean filter, washed with cold pentane, and dried in vacuo at low temperature. This compound was quite pure and could be used for most purposes; yield 0.230 g, 40%. Recrystallization from toluene containing a small amount of phosphine caused partial loss of ethylene and change of the complex, dec pt 98 °C. Anal. Calcd for $C_{14}H_{40}ClN_6P_2Rh$: C, 34.1; H, 8.18; Cl, 7.19; N, 17.0; P, 12.6. Found: C, 34.1; H, 8.2; Cl, 7.10; N, 16.7; P, 12.6. IR: ν(Rh–Cl) at 310 cm^{-1} in Nujol mull.

Effect of Heat on the Previous Reaction. When the preparation of the orange complex previously described was attempted in hot pentane or benzene, different compounds were obtained showing variable N:P ratios according to the temperature and time of reaction. In a typical trial 0.155 g of $[RhCl(C_2H_4)_2]_2$ (0.4 mmol) was dissolved in 30 mL of benzene and added to a benzene solution of the phosphine (0.6 g, 4.4 mmol in 30 mL). The solution was stirred at room temperature and then heated to reflux for 1 h. The solution was concentrated to a small volume, and pentane was added. The yellow compound that precipitated was filtered off and the solution cooled to −20 °C. The yellow crystals formed were filtered off and dried to yield pure $Rh_4Cl_4[(Me_2N)_2P-P(NMe_2)_2]_6$: dec pt 137 °C; yield 20% (0.065 g). ^{1}H NMR: 2.80 (cm) ppm. Anal. Calcd for $C_{60}H_{180}Cl_4N_{30}P_{18}Rh_4$: C, 29.6; H, 7.46; Cl, 5.83; N, 17.3; P, 22.9. Found: C, 29.6; H, 7.25; Cl, 6.06; N, 17.3; P, 23.0. Mol wt in benzene: calcd, 2433, found, 2300.

Recrystallization of the first fraction collected gave pure $RhCl[P(NMe_2)_3][(Me_2N)_2P-P(NMe_2)_2]$, dec pt 143 °C. Anal. Calcd for $C_{14}H_{42}ClN_7P_3Rh$: C, 31.2; H, 7.85; Cl, 6.57; N, 18.16; P, 17.2. Found: C, 30.8; H, 7.81; Cl, 6.80; N, 18.1; P, 17.2. Mol wt in benzene: calcd, 540; found, 500. ^{1}H NMR: 2.84 (m, 18 H), 2.67 (m, 24 H) ppm.

Preparation of $RhCl[P(O_2CNMe_2)(NMe_2)_2]_2 \cdot CO_2$. To a filtered solution of $[RhCl(C_2H_4)_2]_2$ (0.280 g; 0.72 mmol) in toluene (20 mL) was added 0.409 g (2.51 mmol) of $P(NMe_2)_3$ under N_2. The solution was pumped in vacuo for a few seconds, saturated with CO_2, stirred for 1 h at room temperature and concentrated in vacuo to 10 mL. Pentane (5 mL) was added, and the clear yellow solution was cooled to −20 °C. The yellow crystals that separated were filtered off, washed with pentane, and dried in vacuo; dec pt 115 °C. Anal. Calcd for $C_{15}H_{36}ClN_6O_6P_2Rh$: C, 30.2; H, 6.08; Cl, 5.94; N, 14.1; P, 10.4. Found: C, 30.0; H, 6.08; Cl, 6.06; N, 14.1; P, 11.0. Coordinated CO_2: calcd, 7.4; found, 6.6 (by iodine addition at room temperature); 3.4–6.5% (thermal decomposition of the solid sample in vacuo). The amount of CO_2 released by thermal decomposition depends on the rate of rise of the temperature; the higher value is obtained by a sudden heating of the sample at 140 °C.

Preparation of $RhCl[P(O_2CNMe_2)(NMe_2)_2]_2$. To a filtered solution of $[RhCl(C_2H_4)_2]_2$ (0.075 mg; 0.19 mmol) in toluene (10 mL) 0.160 g (0.77 mmol) of $P(O_2CNMe_2)(NMe_2)_2$ was added under nitrogen and the solution stirred for 1 h. A yellow solid began to separate. Pentane was added to complete the precipitation, and the solid was filtered off and washed with pentane. After several crystallizations from cold toluene–pentane pure $RhCl[P(O_2CNMe_2)(NMe_2)_2]_2$ was obtained. Anal. Calcd for $C_{14}H_{36}ClN_6O_4P_2Rh$: C, 30.4; H, 6.56; Cl, 6.41; N, 15.2; P, 11.2. Found: C, 30.5; H, 6.6; Cl, 6.5; N, 15.3; P, 11.0.

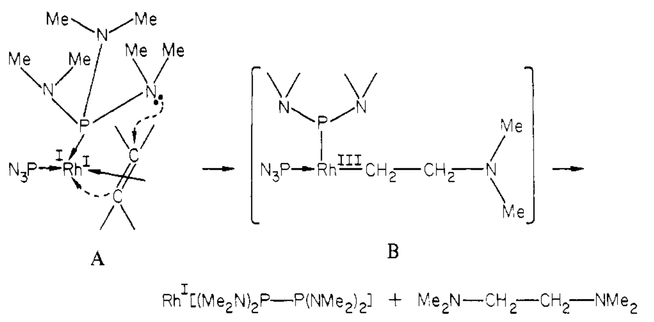
Preparation of the Sample for ^{1}H NMR Spectroscopy. All the samples were prepared at −10 °C and allowed to reach the temperature of the probe (ca. 27 °C) just before the spectrum was run. $CDCl_3$ was used as solvent.

Chromatographic Analyses. The identification of the amines *N,N,N′,N′*-tetramethylhydrazine and *N,N,N′,N′*-tetramethylethylenediamine was carried out by means of TLC [silica gel; 80:20 ethanol:NH_3 (13% w/w water solution) mixture or 80:20:20 *n*-butyl alcohol:ethyl alcohol:NH_3 (13% solution) mixture] or gas chromatography (2-m Carbowax 400 + 8% KOH on Chromosorb; or 2-m Carbosieve + 0.8% KOH).

Results and Discussion

From the reaction of $[RhCl(C_2H_4)_2]_2$ (I) with $P[N(CH_3)_2]_3$ in toluene a variety of compounds can be obtained depending on the solvent used and on the time and temperature of the reaction. At room temperature in toluene under controlled conditions the orange complex $RhCl(C_2H_4)(PN_3)_2$ (II) can be obtained. It is usually contaminated with other complexes showing a N:P ratio lower than 3 (the values more frequently encountered are 2, 1.67, and 1.5). II is stable in the solid state at low temperature but in solution undergoes changes at rates that are dependent on both the temperature and solvent used. The ^{1}H NMR spectrum of the complex in $CDCl_3$ shows a doublet at 2.75 (36 H, J_{H-P} = 8.2 Hz) ppm due to the methyl protons and a singlet at 2.60 (3.5 H) ppm attributed to the coordinated ethylene. The doublet structure of the CH_3 protons shows that the P–P coupling of the two phosphorus ligands through the metal is zero or very small compared to the H–P coupling. This seems to suggest a cis geometry, as the trans arrangement of the phosphines usually produces a higher P–P coupling and the methyl signal is observed as a triplet. The resolution of the signal and the ratio of the intensities of the peaks is dependent on J_{P-P}.[1,4,9] When the solution is aged, its ^{1}H NMR spectrum changes slowly to a multiplet (Figure 1) whose complexity cannot be explained merely on the basis of a cis–trans isomerization of the complex and appearance of a signal due to a $X_nAA'X'_n$ system. It can be inferred that a more complex process takes place in solution. Moreover, when the solution is aged and the ^{1}H NMR spectrum run at temperature lower than 10 °C it is possible to locate new signals at 1.30 (t, *J* = 7 Hz) and 3.70 (m) ppm. These are consistent with the σ-CH_2–CH_2–Rh grouping (compound B in Scheme I) and support the proposed reaction pathway (the triplet at 1.30 ppm is assigned to the Rh–CH_2 methylene group). Compound B is not easily detected at room temperature. Heating the NMR tube at 60–70 °C causes a new change in the spectrum, and the presence of *N,N,N′,N′*-tetramethylethylenediamine (III) can be shown by means of TLC or gas chromatography. The yield is strongly dependent on the rate of change of the temperature. The residual bis(dimethylamino)phosphino moieties couple to give di- or triphosphine compounds, isolated with work on a preparative scale. The existence of possible phosphido complexes of rhodium is ruled out on the basis of the stability to air of the complexes and of their spectral properties. The formation of the triphosphine $(Me_2N)_2P-P(NMe_2)-P(NMe_2)_2$ takes place when the system $[RhCl(C_2H_4)_2]_2-P(NMe_2)_3$ is heated for a long time in boiling benzene. The ligand $(Me_2N)_2P-P(NMe_2)_2$ is formed preferentially in boiling pentane.[11] In the last case, traces of tetramethylhydrazine have been detected in the reaction mixture. The formation of the diphosphine is the first step, and this compound can give further reaction.

Scheme I



The transfer of dimethylamino groups, e.g., to alcohols[12] or to esters,[13] is a characteristic reaction of $P(NMe_2)_3$, but to our knowledge, this is the first example of transfer to olefins.

---

(11) It is difficult to establish unequivocally the experimental conditions for the selective preparation of the dimerized or trimerized phosphorus ligands. The diphosphine and triphosphine are obtained in a mixture and with variable yield.

(12) R. Burgada and H. Normant, *C. R. Hebd. Seances Acad. Sci.*, **257**, 1943 (1963); R. Burgada, *Ann. Chim. (Paris)*, **8**, 347 (1963).

(13) R. Burgada, *C. R. Hebd. Seances Acad. Sci.*, **258**, 1532 (1964).

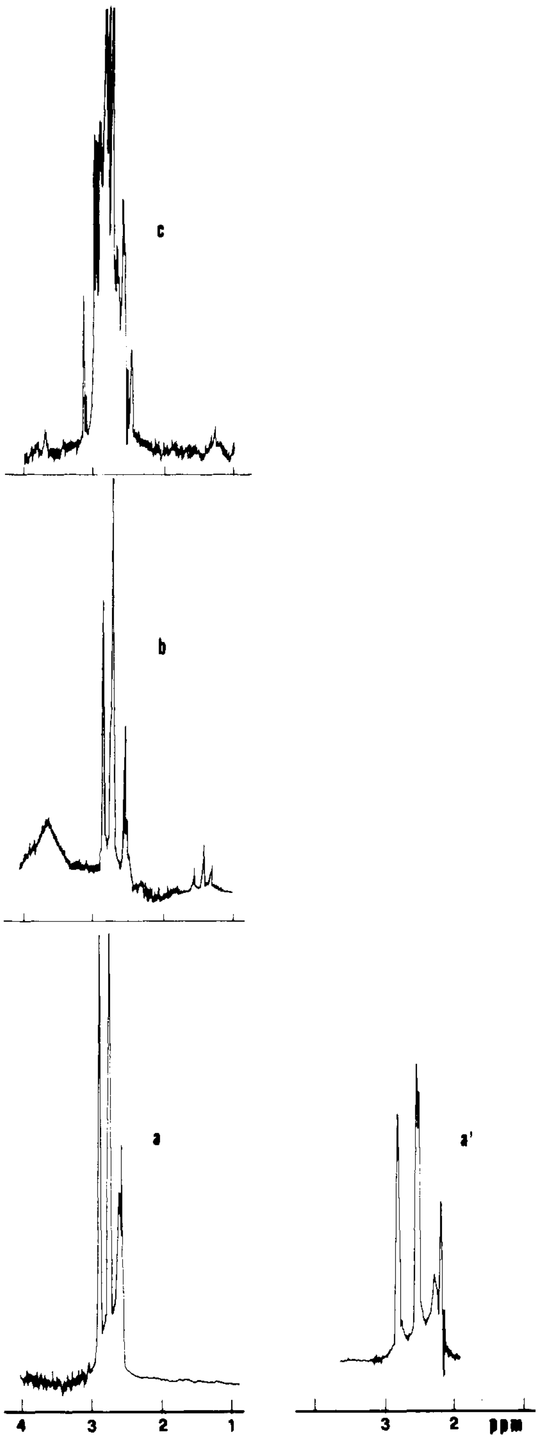


Figure 1. ^1H NMR spectrum of (a) the system $[RhCl(C_2H_4)_2]_2$-$P(NMe_2)_3$ (1:2 molar ratio) recorded 5 min after the addition of the phosphine to the Rh–ethylene complex dissolved in $CDCl_3$ [a′ shows the expansion to 300 Hz; the doublet at 2.67 ppm (J_{P-H} = ca. 10) is due to the free phosphine], (b) the same solution as in (a) aged for 1 h at 0 °C, and (c) the same solution aged for 1 h at 37 °C.

The N_2P-$P(N)$-PN_2 skeleton resembles the $\overline{N{=}P{-}N{=}P{-}N{=}P}{-}P(NMe_2){-}\overline{P{=}N{-}P{=}N{-}P{=}N}$ arrangement formed in the reaction of a bis[cyclotriphosphazenyl]phosphine bis(hydrochloride) derivative with tris(dimethylamino)phosphine.[14] Moreover, polyphosphine systems, not containing N–P bonds, are also formed in the reaction of tetramethyldiphosphine with dimethylphosphine.[15]

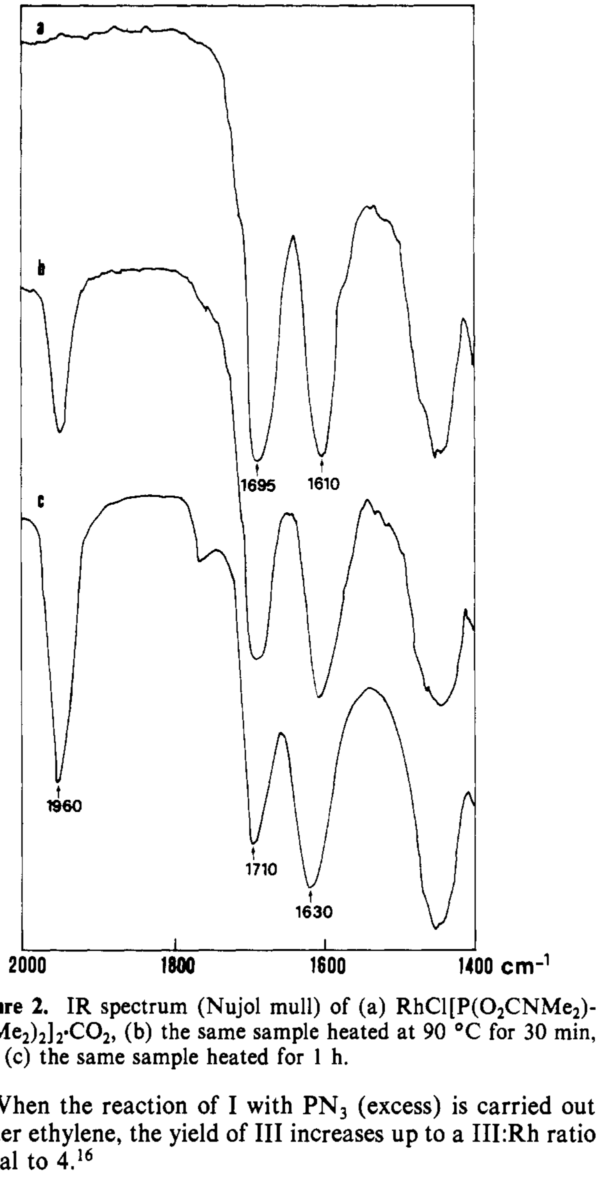


Figure 2. IR spectrum (Nujol mull) of (a) $RhCl[P(O_2CNMe_2)(NMe_2)_2]_2 \cdot CO_2$, (b) the same sample heated at 90 °C for 30 min, and (c) the same sample heated for 1 h.

When the reaction of I with PN_3 (excess) is carried out under ethylene, the yield of III increases up to a III:Rh ratio equal to 4.[16]

From the reaction of I with PN_3 under CO_2 a complex of formula $RhCl[P(O_2CNMe_2)(NMe_2)_2]_2 \cdot CO_2$ (IV) is formed that shows in its IR spectrum (Nujol mull) bands at 1695 (vs) and 1610 (vs) cm^{-1}, attributed to bonded carbon dioxide.

Heating in vacuo of IV at 90 °C causes a partial loss of CO_2 (0.3–0.9 mol CO_2 per mol of Rh; varies with the rate of heating), and the IR spectrum of the residual solid (Nujol mull) shows a decrease of the intensity of the band at 1695 cm^{-1} that shifts moderately toward higher energies. At the same time a new band appears at 1960 cm^{-1}, assigned to a carbonyl group bonded to Rh(I) (Figure 2). Its formation can be explained via oxygen transfer from the coordinated CO_2 to the phosphine that converts into hexamethylphosphorotriamide. The analysis of the IR spectrum shows also the enhancement and broadening of a band present in the spectrum of IV at 1180 cm^{-1} due to the coordination of $(Me_2N)_3P{=}O$ to the metal.[17] At this stage, heating of the complex that still contains bonded CO_2 does not give off carbon dioxide, nor is further conversion to carbonyl observed. These facts suggest two different modes of bonding for CO_2 in IV, i.e., insertion

---

(14) A. Schmidtpeter and J. Högel, *Chem. Ber.*, **111**, 3867 (1978).

(15) K. P. Wanczek, *Z. Naturforsch., A*, **31A**, 414 (1976).

(16) Diphosphines add to olefins or dienes, and the reaction can be promoted both photochemically or thermally: W. Hewertson and I. C. Taylor, *J. Chem. Soc. C*, 1990 (1970); P. Cooper, R. Fields, and R. N. Haszeldine, *ibid.*, 3031 (1971); R. Brandon, R. N. Haszeldine, and P. J. Robinsson, *J. Chem. Soc., Perkin Trans. 2*, 1301 (1973).

(17) M. W. G. De Bolster and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, **90**, 477 (1971).

into the P–N bond and coordination to the metal substrate. The latter would be responsible to the carbonyl formation (both coordination to the metal and interaction with the nitrogen are possible for the nonfixed CO_2).

It is known that CO_2 can insert into the P–N bond of free PN_3 to afford $P(O_2CNMe_2)_x(NMe_2)_{3-x}$ (x = 1, 2).[18] From the reaction of $P(O_2CNMe_2)(NMe_2)_2$ with I we have isolated the complex $RhCl[P(O_2CNMe_2)(NMe_2)_2]_2$ (V) that shows in its IR spectrum in Nujol mull bands at 1710 (s) and 1632 (vs) cm^{-1} due to inserted CO_2. This complex does not afford Rh–carbonyl species on heating up to 150 °C, nor does it liberate carbon dioxide.

That the carbamato species are present in IV and are not formed upon heating is confirmed by the analysis of the ^1H NMR spectrum of IV. The insertion of CO_2 into the P–N bond of PN_3 causes loss of P–H coupling. In fact the compounds $P(O_2CNMe_2)_x(NMe_2)_{3-x}$ present two different proton resonances: a singlet (at 2.96 ppm for both compounds with $x = 1$ and $x = 2$) attributed to the $P(O_2CNMe_2)$ methyls, and a doublet (at 2.75 ppm, $J_{P-H} = 9.8$, for $x = 1$; 2.66 ppm, $J_{P-H} = 10.2$, for $x = 2$) due to the $P(NMe_2)$ methyl groups.

The ^1H NMR sectrum of IV presents a singlet at 2.98 ppm and a triplet centered at 2.80 ppm, $J = 10.2$, with an intensity ratio 1:2.[19] Aging the solution causes change of the spectrum to a complex multiplet, and the complexes isolated at this stage present a N:P ratio lower than 3.

Attempts to obtain IV from V and CO_2 afforded impure material as a carbonyl complex was formed.[20]

Such an insertion of CO_2 into the P–N bond of the coordinated phosphine takes place also when the complex $Pd_2Cl_4[P(NMe_2)_3]_2$ is exposed to carbon dioxide in a THF solution. The white compound formed shows IR bands at 1710 (s) and 1620 (vs) cm^{-1} (Nujol mull).[21]

Further study is in progress in order to elucidate the mode of bonding of the coordinated CO_2 in these and related complexes.

Acknowledgment. Financial support from CNR, Rome, is gratefully acknowledged.

Registry No. I, 12081-16-2; II, 79255-72-4; III, 110-18-9; IV, 79255-73-5; V, 79255-74-6; $RhCl[P(NMe_2)_3][Me_2N)_2P-P(NMe_2)_2]$, 79255-75-7.

---

(18) G. Oertel, H. Malz, and H. Holtschmidt, *Chem. Ber.*, **97**, 891 (1964).

(19) The triplet structure suggests a P–P coupling through the metal. A similar pattern is presented by the compound $RhCl[P(O_2CNMe_2)(NMe_2)_2]_2$: singlet at 3.1 ppm and triplet at 3.0 ppm, $J_{P-H} = 10.7$.

(20) The rate of reaction of IV with CO_2 is quite slow, and the reduction to CO takes place also at −20 °C.

(21) Once isolated from the solution, the white complex decomposes easily at −10 °C, and this prevented its full characterization.

Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

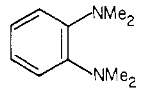
Unsymmetrical Cleavage Reaction of μ-(Dimethylamino)diborane(6)

Philip C. Keller

Received April 21, 1981

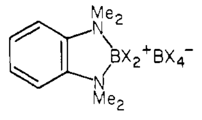
The literature contains a number of reports on reactions of μ-aminodiboranes with ammonia,[1,2] primary,[3] secondary,[3] and teritary amines,[1,2,4] phosphines,[5] methyl isocyanate,[6] sodium hydride,[7] etc. In all cases, the products are simple 1:1 adducts of the form (donor)–BH_2–NR_2–BH_3 (although in the case of methyl isocyanate a subsequent hydroboration occurs[6]). There are no known examples of the formation of ionic "unsymmetrical cleavage"[8] products with μ-aminodiboranes, although reactions of this type are not uncommon in the acid–base chemistry of diborane(6).[9]

In recent papers we reported that the bidentate base *N*,*N*,*N'*,*N'*-tetramethyl-*o*-phenylenediamine (TMPD) reacts with

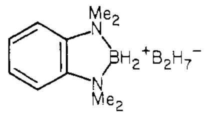


TMPD

boron trichloride and trifluoride[10] and with diborane(6)[11] to give ionic products I or II.



I, X = H, Cl, F

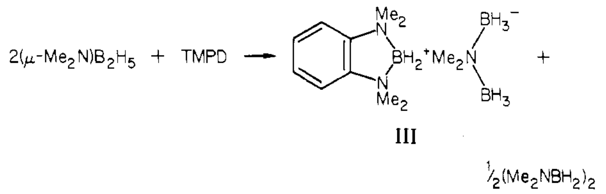


II

The ortho substitution of the amino groups in TMPD and the bulk of the *N*-methyl substituents appear to strongly favor a chelating coordination of BX_2^+ (X = H, Cl, F). In this paper we describe the action of TMPD on $(\mu\text{-}Me_2N)B_2H_5$ to give the first example of the formation of unsymmetrical cleavage products with a μ-aminodiborane(6).

Results and Discussion

Over a period of 10–20 days, TMPD reacts with excess $(\mu\text{-}(CH_3)_2N)B_2H_5$ in diethyl ether or monoglyme according to eq 1. The ionic product III is insoluble in either solvent and crystallizes as the reaction proceeds. In one experiment in which the reaction was monitored at 1–5-day intervals by boron-11 NMR spectroscopy, the spectra showed only a steadily diminishing $(\mu\text{-}Me_2N)B_2H_5$ signal and a steadily increasing sharp triplet due to $(Me_2NBH_2)_2$. No intermediate species or other byproducts could be detected.



III

(1)

The product III exhibits the spectral properties expected of a salt of the known $(TMPD)BH_2^+$ and $Me_2N{\cdot}2BH_3^-$ ions.[7,11] The boron-11 NMR spectrum in CH_2Cl_2 consists of a broad triplet of unit intensity (δ 6.1, J = 118 Hz, cation) and a quartet of intensity 2 (δ −11.2, J = 91 Hz, anion) in good agreement with published data for these species.[7,11] The infrared spectrum is essentially a superposition of the absorptions of the component ions with a few minor shifts. The salt is

---

(1) Schlesinger, H. I.; Ritter, D. M.; Burg, A. B. *J. Am. Chem. Soc.* **1938**, *60*, 2297.

(2) Burg, A. B.; Randolph, C. L., Jr. *J. Am. Chem. Soc.* **1949**, *71*, 3451.

(3) Hahn, G. A.; Schaeffer, R. **1964**, *86*, 1503.

(4) Burg, A. B.; Kuljian, E. S. **1950**, *72*, 3103.

(5) Burg, A. B.; Sandlin, J. S. *Inorg. Chem.* **1965**, *4*, 1467.

(6) Molinelli, R.; Smith, S. R.; Tanaka, J. *J. Chem. Soc., Dalton Trans.* **1972**, 1363.

(7) Keller, P. C. *Inorg. Chem.* **1971**, *10*, 2256.

(8) Parry, R. W.; Edwards, L. J. *J. Am. Chem. Soc.* **1959**, *81*, 3554.

(9) Shore, S. G. In "Boron Hydrides"; Muetterties, E. L., Ed.; Academic Press: New York, 1978; p 79.

(10) Axtell, D. D.; Cambell, A. C.; Keller, P. C.; Rund, J. V. *J. Coord. Chem.* **1976**, *5*, 129.

(11) Keller, P. C.; Rund, J. V. *Inorg. Chem.* **1979**, *18*, 3197.