

at the University of Michigan, Ann Arbor. The authors are also grateful for support by the National Science Foundation under Grant GP-14873 to the University of Utah, and to Professor William Jolly of the University of California at Berkeley for helpful discussion.

Registry No. Ammonia, 7664-41-7; methylamine, 74-89-5; dimethylamine, 124-40-3; H_3PBH_3 , 15120-00-0; $K[H_2PBH_3]$, 56942-31-5; $Na[H_2PBH_3]$, 56942-32-6; $Li[H_2PBH_3]$, 34390-49-3.

References and Notes

- (1) (a) J. W. Gilje, K. W. Morse, and R. W. Parry, *Inorg. Chem.*, **6**, 1761 (1967); (b) E. L. Gamble and P. Gilmont, *J. Am. Chem. Soc.*, **62**, 717 (1940).
- (2) (a) H. I. Schlesinger and A. B. Burg as communicated in a footnote to a paper by E. L. Gamble and P. Gilmont, ref 1b; (b) H. I. Schlesinger and A. B. Burg, *Chem. Rev.*, **31**, 1 (1942).
- (3) (a) K. W. Morse and R. W. Parry, 152nd National Meeting of the American Chemical Society, New York, N.Y., Sept 1966, Inorganic Division paper No. 43; (b) K. W. Morse, Ph.D. Dissertation, The University of Michigan, Ann Arbor, Mich., 1966, p 27.
- (4) R. W. Rudolph, R. W. Parry, and C. J. Farran, *Inorg. Chem.*, **5**, 723 (1966).
- (5) We thank a helpful referee who pointed out that the decrease in J_{B-H} when H_3PBH_3 is converted to $H_2PBH_3^-$ may be rationalized as a lone pair effect through an extrapolation of the C-H coupling arguments of V. M. S. Gil and A. C. P. Alves, *Mol. Phys.*, **16**, 527 (1969); V. M. S. Gil and J. J. C. Teixeira-Dias, *ibid.*, **15**, 47 (1968).
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- (7) In our hands at -78° this reaction goes as indicated. N. R. Thompson, *J. Chem. Soc.*, 6290 (1965), working at -33° rather than -78° , reported the formation of $K[H_2NBH_3]$ rather than the anticipated $K[H_2PBH_3]$. As reported here, we found increasing amounts of H_3NBH_3 at -33° and above (step 3); this fact correlates with Thompson's observation, since $K[H_2NBH_3]$ would form from H_3NBH_3 . (Temperature is important in the reaction of K with H_3PBH_3 .)
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- (11) While this assumption may sound somewhat arbitrary, it has some precedent in that the activity coefficients of species in water solution may become much larger than 1.0 as the concentration or the ionic strength of the solution increases.
- (12) Ammonia is a stronger base toward BH_3 than is phosphine. Proton affinities provide one estimate of relative base strengths toward a "hard acid": $NH_3 = 207$ kcal/mol, M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2028 (1969); $PH_3 = 186$ kcal/mol, D. Holtz and J. L. Beauchamp, *J. Am. Chem. Soc.*, **91**, 4328 (1969).
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Phosphorus-Substituted Hydrazines. III. Group 6B Metal Carbonyl Derivatives of Selected Phosphinohydrazines¹

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Reactions of the group 6B metal carbonyls with the phosphinohydrazines *N*-diphenylphosphino-*N,N*-dimethylhydrazine (DMPH), diphenylphosphinotrimethylhydrazine (TMPH), and *N,N*-bis(diphenylphosphino)-*N,N*-dimethylhydrazine (DPH) have yielded several new derivatives: $M(CO)_5(L)$, $M = Cr, Mo,$ and W and $L = DMPH, TMPH,$ and DPH ; *cis*- and *trans*- $M(CO)_4(DMPH)_2$, $M = Cr, Mo,$ and W ; *trans*- $M(CO)_4(TMPH)_2$, $M = Cr, Mo,$ and W ; *cis*- $M(CO)_4(DPH)$, $M = Cr, Mo,$ and W ; $M(CO)_4(TMPH)$, $M = Cr, Mo,$ and W ; *cis*- $M(CO)_3(DMPH)_3$, $M = Mo$ and W ; $M(CO)_3(TMPH)_2$, $M = Mo$ and W . The nature of the phosphinohydrazine to metal bonding could be ascertained effectively from an analysis of the $\nu(CO)$ and $\nu(NH)$ stretching frequencies in the infrared and the proton and phosphorus NMR data. Although phosphorus to metal bonding was always evident, chelation involving the terminal amine group occurred in the $M(CO)_4(TMPH)$ and $M(CO)_3(TMPH)_2$ derivatives.

Introduction

Mono- and polydentate, trivalent group 5A ligands, particularly amines and phosphines, are quite numerous and because of their many structural variations exhibit a diversity of electronic and steric properties. Most commonly, chelating agents have been designed with Lewis base centers located strategically along a carbon chain or in ortho ring positions. Being a rather unique chelating system involving two bonded nitrogen atoms, phosphinohydrazines offer a variety of potential bonding activities.¹⁻⁵ Examples in the P-N(P)-N unit include unidentate bonding through one of the four donor sites, chelation to a metal through the two phosphorus atoms or one phosphorus and a nitrogen, and bridging between two different metal centers. Although previous studies indicate that phosphorus centers are more basic toward low valent metal atoms than are amine groups,² evidence of nitrogen chelation has been cited.⁴ As part of a program to ascertain the nature and extent of phosphinohydrazine interactions with transition

metal systems, we shall describe results of group 6B metal carbonyl reactions with selected ligands.

Experimental Section

Microanalyses and molecular weights were performed by M-H-W Laboratory, Garden City, Mich. Infrared spectra were recorded in methylene chloride or methylcyclohexane solutions and KBr pellets on a Model 621 Perkin-Elmer spectrometer. Proton NMR spectra were taken on Varian Associates Model T-60 and HA-100 instruments in chloroform-*d* with tetramethylsilane as an internal standard. Phosphorus NMR spectra were obtained on the HA-100 instrument operating at 40.5 MHz with 85% H_3PO_4 as an external standard. Melting points were taken in open capillaries and are uncorrected. Dry nitrogen was used routinely for deaeration of solvents, maintenance of an inert atmosphere over reaction mixtures, and admission to evacuated vessels. Analytical data and physical properties of the new phosphinohydrazine metal carbonyl derivatives are contained in Table I.

Reagents. Chemicals were obtained from the following sources: chlorodiphenylphosphine and metal hexacarbonyls (Pressure Chemical

Table I. Analytical Data and Physical Properties of Phosphinohydrazine Metal Carbonyls

Compd ^a	Color	Mp, °C ^b	Yield, %	Anal. calcd (found), %				Mol wt ^c
				C	H	N	P	
<i>trans</i> -Cr(CO) ₄ (DMPH) ₂	Pale yellow	156–157 dec	87	58.89 (58.72)	5.25 (5.54)	8.58 (8.31)	9.49 (9.27)	652 (670)
<i>cis</i> -Mo(CO) ₄ (DMPH) ₂	White	148–150 dec	75	55.17 (55.08)	4.90 (4.76)	8.04 (7.77)	8.90 (8.60)	696 (720)
<i>cis</i> -W(CO) ₄ (DMPH) ₂	Yellow	155–157 dec	75	48.99 (48.75)	4.36 (4.71)	7.14 (6.85)	7.89 (7.80)	784 (800)
<i>cis</i> -Mo(CO) ₃ (DMPH) ₃	White	163–165	89	59.21 (58.87)	5.60 (5.50)	9.21 (9.11)	10.20 (9.90)	912 (900)
<i>cis</i> -W(CO) ₃ (DMPH) ₃	White	175–177 dec	86	54.01 (53.86)	5.14 (5.30)	8.40 (8.17)	9.28 (9.85)	1001 (1010)
Cr(CO) ₅ (DPH)	White	132–133	13	60.00 (60.16)	4.22 (3.98)	4.52 (4.42)	9.98 (10.07)	620 (590)
Mo(CO) ₅ (DPH)	White	129–130	7	56.04 (56.05)	3.94 (3.68)	4.22 (3.98)	9.32 (9.11)	664 (630)
Cr(CO) ₄ (DPH)	Yellow	214–216	63	60.81 (60.93)	4.39 (4.17)	4.72 (4.78)	10.47 (10.30)	592 (575)
Mo(CO) ₄ (DPH)	Yellow	198–199 dec	62	56.60 (56.42)	4.08 (3.98)	4.40 (4.16)	9.75 (9.46)	636 (600)
W(CO) ₄ (DPH)	Yellow	204–205 dec	89	49.74 (49.68)	3.61 (3.36)	3.86 (3.71)	8.55 (8.60)	724 (710)
Cr(CO) ₅ (TMPH)	White	124–127 dec	8	53.34 (53.41)	4.25 (4.23)	6.22 (5.91)	6.88 (6.75)	450 (430)
Mo(CO) ₅ (TMPH)	White	103–106 dec	46	48.59 (48.51)	3.87 (3.95)	5.66 (5.55)	6.26 (5.99)	494 (480)
W(CO) ₅ (TMPH)	White	113–117 dec	24	41.26 (41.64)	3.29 (3.31)	4.81 (4.58)	5.32 (5.50)	582 (590)
<i>trans</i> -Cr(CO) ₄ (TMPH) ₂ ^d	Yellow	148–150 dec	45	54.91 (54.72)	5.27 (4.98)	7.32 (7.08)	8.09 (8.37)	765 (750)
<i>trans</i> -W(CO) ₄ (TMPH) ₂ ^d	Yellow	171–174 dec	40	46.84 (46.61)	4.49 (4.27)	6.24 (5.92)	6.90 (7.05)	897 (879)
Cr(CO) ₄ (TMPH)	Yellow	119–121 dec	45	54.03 (54.09)	4.53 (4.39)	6.63 (6.44)	7.33 (7.16)	422 (430)
W(CO) ₄ (TMPH)	Yellow	138–141 dec	21	41.18 (41.08)	3.45 (3.23)	5.05 (4.94)	5.59 (5.48)	554 (545)
W(CO) ₃ (TMPH) ₂	Cream	80 dec	80	50.52 (50.69)	4.88 (4.83)	7.14 (7.13)	7.89 (7.76)	784 (776)

^a DMPH = *N*-diphenylphosphino-*N'*,*N'*-dimethylhydrazine; DPH = bis(diphenylphosphino)-*N'*,*N'*-dimethylhydrazine; TMPH = diphenylphosphinotrimethylhydrazine. ^b Dec is decomposition. ^c Determined by vapor-phase osmometry at 37° in CHCl₃. ^d Isolated as CH₂Cl₂ adducts.

Company); 2,5-norbornadiene (Nbd), 1,3-tetramethylpropylenediamine (Tmpa), and cycloheptatriene (Cht) (Aldrich Chemical Co.). Florisil (60–100 mesh) used for column chromatography was obtained from Fisher Scientific Co. The metal carbonyl substrates Cr(CO)₄(Nbd),⁶ Mo(CO)₄(Nbd),⁷ W(CO)₄(Tmpa),⁸ and M(CO)₃(Cht)⁹ (M = Cr, Mo, and W), the catalyst (C₂H₅)₃OBF₄,¹⁰ and the ligands⁵ *N*-diphenylphosphino-*N'*,*N'*-dimethylhydrazine (DMPH), diphenylphosphinotrimethylhydrazine (TMPH), and *N,N*-bis(diphenylphosphino)-*N'*,*N'*-dimethylhydrazine (DPH) were synthesized according to literature procedures.

Syntheses. M(CO)₅(L) (M = Cr, Mo, and W and L = DMPH, TMPH, and DPH). Equimolar amounts of (C₂H₅)₄N[M(CO)₅Br]¹¹ and ligand each dissolved in CH₂Cl₂ were mixed and a slurry of AgNO₃ or (C₂H₅)₃OBF₄ in CH₂Cl₂ was immediately added.¹² After stirring at ambient temperatures for 0.5 to 24 hr (longer times with tungsten) the solution was filtered and the solvent evaporated (25° (40 mm)). The residue was heated (55° (0.05 mm)) for 2 days to remove M(CO)₆ impurities, extracted with CH₂Cl₂, placed on a Florisil column, and eluted with CH₂Cl₂ or pentane–CH₂Cl₂ mixtures. Evaporation of the eluant followed by two recrystallizations from hexane yielded pure crystals.

cis, *trans*-M(CO)₄(DMPH)₂. Mo(CO)₄(Nbd) (0.50 g, 1.67 mmol) and DMPH (0.86 g, 3.53 mmol) were stirred in methylcyclohexane for 1.5 hr at 25°. The solvent was evaporated and the residue was recrystallized from CH₂Cl₂–hexane. The predominantly *cis* isomeric mixture could not be completely separated. The chromium and tungsten analogues were synthesized similarly (Cr(CO)₄(Nbd) and DMPH in methylcyclohexane at 100° for 1 hr; W(CO)₄(Tmpa) and DMPH in CHCl₃ at 61° for 3 hr).

cis-M(CO)₃(DMPH)₃ (M = Mo and W). M(CO)₃(Cht) (1.88 mmol) and DMPH (5.84 mmol) were stirred in methylcyclohexane at 25° for 10 min. The precipitate was filtered and recrystallized from CH₂Cl₂–hexane to yield white crystals. The analogous chromium

reaction yielded only *trans*-Cr(CO)₄(DMPH)₂.

M(CO)₄(DPH) (M = Cr, Mo, and W). Mo(CO)₄(Nbd) (1.0 g, 3.33 mmol) and DPH (1.43 g, 3.34 mmol) were stirred in methylcyclohexane at 25° for 9 hr. Following solvent evaporation the residue was dissolved in CH₂Cl₂, placed on a Florisil column, and eluted with CH₂Cl₂. Eluant evaporation and recrystallization from CH₂Cl₂–hexane produced pure crystals. The chromium and tungsten complexes were prepared as follows: Cr(CO)₄(Nbd) and DPH in methylcyclohexane at 100° for 2 hr; W(CO)₄(Tmpa) and DPH in CHCl₃ at 61° for 1 hr.

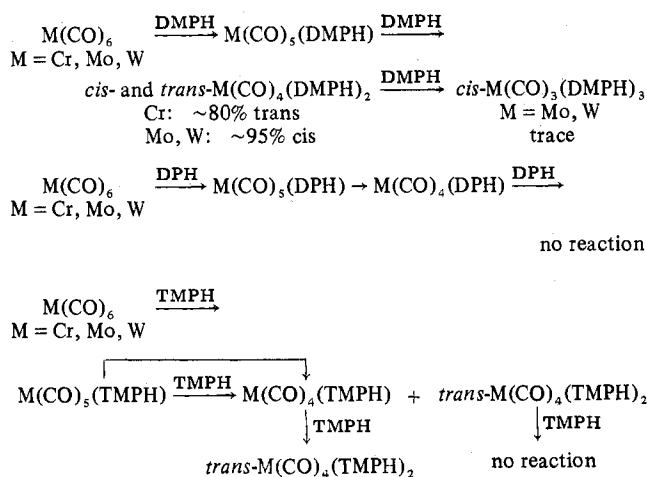
M(CO)₄(TMPH) and *trans*-M(CO)₄(TMPH)₂ (M = Cr, Mo, and W). Cr(CO)₄(Nbd) (0.45 g, 1.76 mmol) and TMPH (0.92 g, 3.57 mmol) were refluxed in benzene for 4 hr and then the solvent was removed (25° (0.001 mm)). Fractional crystallization from CH₂Cl₂–hexane proved effective in separating Cr(CO)₄(TMPH) (less soluble) and *trans*-Cr(CO)₄(TMPH)₂–CH₂Cl₂. Although the tungsten products could be synthesized by the procedure described for those of chromium, the molybdenum complexes could never be completely separated and purified.

W(CO)₃(TMPH)₂. W(CO)₃(Cht) (0.50 g, 1.39 mmol) and TMPH (1.09 g, 4.23 mmol) were stirred in benzene at 25° for 20 min. Addition of heptane followed by solvent reduction caused precipitation. The filtered product was then recrystallized from benzene. Mo(CO)₃(TMPH)₂ was unstable and converted readily to Mo(CO)₄(TMPH) in solution. Only *trans*-Cr(CO)₄(TMPH)₂ resulted from the Cr(CO)₃(Cht)–TMPH reaction.

Results and Discussion

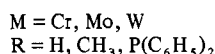
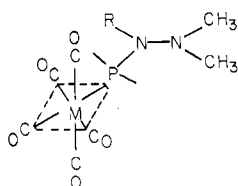
When the group 6B metal carbonyls were allowed to interact with the phosphinohydrazines *N*-diphenylphosphino-*N'*,*N'*-dimethylhydrazine (DMPH), diphenylphosphinotrimethylhydrazine (TMPH), and *N,N*-bis(diphenylphosphino)-*N'*,

Scheme I



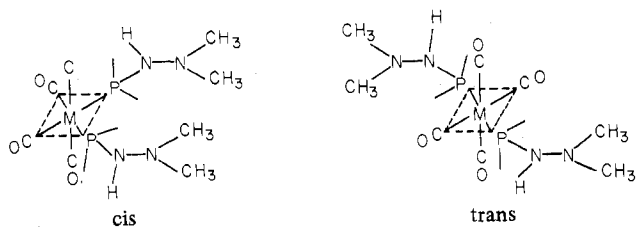
N'-dimethylhydrazine (DPH), a rather diverse sequence of reactions (Scheme I) was observed depending upon the particular metal and ligand system studied.

Reactions of all three ligands with each metal hexacarbonyl resulted in monosubstituted derivatives exhibiting phosphorus to metal bonding. These pentacarbonyls, however, could be

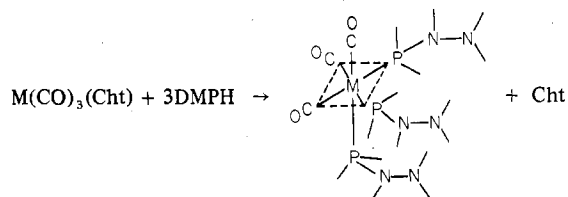


synthesized in better yields by utilizing the $[\text{M}(\text{CO})_5\text{Br}]^-$ /ligand indirect route.¹² Allowing $\text{M}(\text{CO})_5(\text{DMPH})$ species and $\text{M}(\text{CO})_6$ to interact in decalin at 160° for 4 days failed to promote nitrogen to metal bond formation either through chelation to the same metal or bridging to two different metal centers.

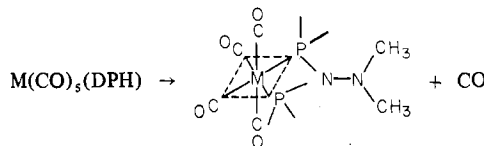
Subsequent reactions of $\text{M}(\text{CO})_5(\text{ligand})$ with additional ligand yielded a variety of products. A cis-trans mixture of disubstituted tetracarbonyls, $\text{M}(\text{CO})_4(\text{DMPH})_2$, resulted from the $\text{M}(\text{CO})_5(\text{DMPH})$ and DMPH reactions although the trans isomer was most predominant for chromium and the cis for molybdenum and tungsten. Apparently, in the chromium complex steric effects are more important than those electronic



ones which favor cis formation. Again, the most effective preparative procedure for these $\text{M}(\text{CO})_4(\text{ligand})_2$ species was the $\text{M}(\text{CO})_4(\text{norbornadiene})/\text{ligand}$ route. All attempts to encourage further carbonyl replacement by allowing the $\text{M}(\text{CO})_4(\text{DMPH})_2$ species and DMPH to reflux in methylcyclohexane at 100° for 1 week yielded only trace quantities of *cis*- $\text{Mo}(\text{CO})_3(\text{DMPH})_3$. However, the tricarbonyls *cis*- $\text{M}(\text{CO})_3(\text{DMPH})_3$ ($\text{M} = \text{Mo}$ and W) could be effectively synthesized by taking advantage of the lability of $\text{M}(\text{CO})_3(\text{Cht})$ ($\text{Cht} = \text{cycloheptatriene}$).

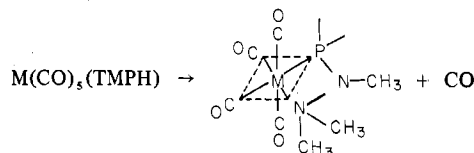


The bisphosphinohydrazine pentacarbonyl derivatives convert smoothly to chelated tetracarbonyls. Evidently steric



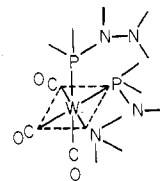
hindrance prohibits further carbonyl replacement with additional DPH even under exposure to rather stringent reaction conditions.

The behavior of TMPH with the group 6 metal carbonyls and their derivatives represented the most interesting aspect of this particular study. All three $\text{M}(\text{CO})_5(\text{TMPH})$ species yielded chelated tetracarbonyl complexes when heated in toluene for 24 hr. When the pentacarbonyls were allowed to



interact with an additional mole of ligand, an approximately equal distribution of chelate $\text{M}(\text{CO})_4(\text{TMPH})$ and *trans*- $\text{M}(\text{CO})_4(\text{TMPH})_2$ resulted.

With 1 mol of *trans*- $\text{M}(\text{CO})_4(\text{TMPH})$ species converted easily to *trans*- $\text{M}(\text{CO})_4(\text{TMPH})_2$ which remained unchanged even in refluxing xylene with additional TMPH. However, $\text{W}(\text{CO})_3(\text{Cht})$ reacted with TMPH (3 mol) to yield the isolable *cis*- $\text{W}(\text{CO})_3(\text{TMPH})_2$ complex. The analogous



molybdenum product could be detected by infrared but changed readily to $\text{Mo}(\text{CO})_4(\text{TMPH})$. Only *trans*- $\text{Cr}(\text{CO})_4(\text{TMPH})_2$ resulted from the $\text{Cr}(\text{CO})_3(\text{Cht})/\text{TMPH}$ reaction.

Spectral Data. Phosphorus to metal bonding in the nine monomeric group 6B metal derivatives is supported by infrared (Table II) and proton and phosphorus NMR data (Table III). Values for the metal carbonyl stretching frequencies correlate well with those for the analogous triphenylphosphine complex and are higher than those for the corresponding nitrogen bonded pyridine molecule. As the metal $\nu(\text{CO})$ stretching frequencies are a measure of the effectiveness of ligands in removing charge from the metal and thus from the carbonyl groups, an order $\text{DMPH} > \text{TMPH} \sim (\text{C}_6\text{H}_5)_3\text{P} > \text{DPH}$ is prevalent in all three metal systems. The carbonyl stretching frequencies routinely follow the sequence $\text{Mo} > \text{W} \geq \text{Cr}$ for an analogous series of complexes.

Relative to the free ligand there is increased shielding in $\tau(\text{CH}_3)$ in the pentacarbonyls indicating an absence of nitrogen bond formation,⁴ there is a $\nu(\text{NH})$ shift to higher frequencies suggesting a lack of internal nitrogen coordination in the DMPH complexes,⁴ and there is decreased shielding of the phenyl protons indicating charge removal from the phosphorus

Table II. Infrared Spectral Data of Phosphinohydrazine Metal Carbonyls and Related Derivatives

Compd	$\nu(\text{CO}), \text{cm}^{-1}$ ^a				$\nu(\text{NH}), \text{cm}^{-1}$ ^b
Cr(CO) ₅ (DMPH)	2070 (w)	1985 (vw)	1951 (sh)	1938 (vs)	3289 (w)
Mo(CO) ₅ (DMPH)	2081 (w)	1993 (vw)	1955 (sh)	1946 (vs)	3273 (w)
W(CO) ₅ (DMPH)	2077 (w)	1983 (vw)	1950 (sh)	1938 (vs)	3288 (w)
Cr(CO) ₅ (DPH)	2061 (w)	1972 (vw)	1936 (sh)	1930 (s)	
Mo(CO) ₅ (DPH)	2072 (w)	1979 (vw)	~1933	1933 (s)	
W(CO) ₅ (DPH)	2070 (w)	1978 (vw)	~1931	1931 (s)	
Cr(CO) ₅ (TMPH)	2067 (w)	1979 (vw)	~1939	1939 (s)	
Mo(CO) ₅ (TMPH)	2076 (w)	1984 (vw)	~1943	1943 (s)	
W(CO) ₅ (TMPH)	2076 (w)	1977 (vw)	~1937	1937 (s)	
Mo(CO) ₅ [P(C ₆ H ₅) ₃] ^c	2075 (w)	1989 (vw)	1950 (s)	1945 (s)	
Mo(CO) ₅ (C ₄ H ₅ N) ^e	2074 (w)		1943 (vs)	1922 (s)	
<i>trans</i> -Cr(CO) ₄ (DMPH) ₂	2015 (vw)	1949 (w)	1895 (vs)		3280 (w)
<i>trans</i> -Cr(CO) ₄ (TMPH) ₂	2014 (vw)	1941 (w)	1890 (vs)		
<i>trans</i> -Mo(CO) ₄ (TMPH) ₂		1950 (w)	1902 (vs)		
<i>trans</i> -W(CO) ₄ (DMPH) ₂		1951 (w)	1893 (vs)		
<i>trans</i> -W(CO) ₄ (TMPH) ₂		1941 (w)	1893 (vs)		
<i>trans</i> -Mo(CO) ₄ [P(C ₆ H ₅) ₃] ₂ ^d		1952 (w)	1903 (vs)		
<i>cis</i> -Cr(CO) ₄ (DMPH) ₂	2015 (m)	1920 (s)	~1895	1895 (s)	3297 (w)
<i>cis</i> -Mo(CO) ₄ (DMPH) ₂	2031 (m)	1935 (s)	1909 (vs)	~1900	3262 (w)
<i>cis</i> -W(CO) ₄ (DMPH) ₂	2026 (m)	1926 (s)	1899 (vs)	~1892	3265 (w)
Cr(CO) ₄ (DPH) ^e	2011 (m)	1917 (sh)	1891 (s)	1870 (sh)	
Mo(CO) ₄ (DPH) ^e	2025 (m)	1923 (sh)	1903 (s)	1892 (sh)	
Mo(CO) ₄ (DPH)	2032 (m)	1940 (s)	1916 (vs)	~1916	
W(CO) ₄ (DPH) ^e	2022 (m)	1916 (sh)	1894 (s)	1884 (sh)	
Cr(CO) ₄ (TMPH) ^e	2012 (m)	1894 (sh)	1880 (vs)	1852 (s)	
Mo(CO) ₄ (TMPH) ^e	2023 (m)	1916 (s)	1899 (vs)	1859 (s)	
W(CO) ₄ (TMPH) ^e	2018 (m)	1891 (sh)	1883 (vs)	1850 (s)	
Mo(CO) ₄ (diphos) ^{e,f}	2020 (m)	1919 (sh)	1907 (vs)	1881 (s)	
Mo(CO) ₄ (N-P) ^{e,g}	2019 (m)	1905 (s)	1893 (s)	1849 (s)	
Mo(CO) ₄ (tmen) ^{e,h,i}	2013 (m)	1890 (s)	1875 (vs)	1837 (s)	
Mo(CO) ₃ (DMPH) ₃ ^e	1943 (s)	1848 (s)			3188 (w)
W(CO) ₃ (DMPH) ₃ ^e	1941 (s)	1845 (s)			3192 (w)
Mo(CO) ₃ (triphos) ^{e,j}	1942 (s)	1848 (s)			
Mo(CO) ₃ (TMPH) ₂ ^e	1926 (s)	1830 (s)	1802 (s)		
W(CO) ₃ (TMPH) ₂ ^e	1922 (s)	1822 (s)	1797 (s)		
Mo(CO) ₃ (diphos)(C ₆ H ₁₁ NH ₂) ^{e,i}	1929 (s)	1836 (s)	1802 (s)		
Mo(CO) ₃ (phen)[P(C ₆ H ₅) ₃] ^{e,k}	1919 (s)	1820 (s)	1788 (s)		
DMPH					3190 (w)

^a Run in methylcyclohexane solutions unless otherwise noted; key to intensities: vw = very weak, w = weak, m = medium, sh = shoulder, s = strong, vs = very strong. ^b Run in potassium bromide pellets. ^c Run in hexane solutions: D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 959 (1968). ^d Run in saturated hydrocarbon solution: R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1301 (1962). ^e Run in chlorinated hydrocarbon solutions. ^f diphos = (C₆H₅)₂PC₂H₄P(C₆H₅)₂: J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961). ^g N-P = (C₆H₅)₂PC₂H₄N(C₂H₅)₂: G. R. Dobson, R. C. Taylor, and T. D. Walsh, *Inorg. Chem.*, **6**, 1929 (1967). ^h tmen = (CH₃)₂NC₂H₄N(CH₃)₂. ⁱ G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, **1**, 287 (1967). ^j triphos = [(C₆H₅)₂PC₂H₄]₂P(C₆H₅)₂: R. B. King et al., *Inorg. Chem.*, **10**, 1841 (1971). ^k phen = 1,10-phenanthroline: L. W. Houk and G. R. Dobson, *J. Chem. Soc.*, 317 (1966).

atom, but the most convincing argument for phosphorus to metal bonding lies in the marked downfield shift in the ³¹P resonance upon ligand chelation.¹³⁻²¹ As often observed in transition metal derivatives of phosphorus ligands, the ³¹P shift in phosphinohydrazine metal carbonyls is in the order Cr > Mo > W.¹³⁻²¹ Because of solubility and quantity limitations phosphorus NMR spectra could not be obtained on several compounds.

Once the lone pair of electrons on the phosphorus atom becomes localized in bond formation, coupling of the ³¹P nucleus with the proton bound to the nitrogen in DMPH increases from 11 to 27 Hz. Similar results are seen in the TMPH derivatives where *J*(³¹P-H) increases for the methyl protons on the same nitrogen with the phosphorus atom and there is no evidence of coupling across the hydrazine linkage. However, phosphorus coupling with the methyl protons across the hydrazine bond, displayed as a *doublet* [*J*(³¹P-H) = 11.5 Hz] that remained unaltered when recorded at 60 and 100 MHz, was observed in the M(CO)₅(DPH) derivatives. This unexpected methyl equivalency may be the result of a rapid rotation-inversion process or an accidental degeneracy. Both the free DPH and the ligand chelated through the two phosphine groups to the same metal center exhibit no phosphorus to methyl proton coupling.

The metal carbonyl stretching frequencies recorded for the M(CO)₄(L)₂ species, where L = DMPH and TMPH, in both

the *cis* and *trans* configuration are consistent with the number and intensity of bands observed for analogous disubstituted phosphine derivatives. As with the pentacarbonyls, *J*(³¹P-N-H) increases markedly from the free ligand value of 11 to 33 Hz. Again, there is no coupling across the N-N bond between the phosphorus atom and the methyl protons in either the DMPH or TMPH compounds. However, in the three *trans*-M(CO)₄(TMPH)₂ derivatives the PN-methyl protons appear as an apparent triplet²²⁻²⁵ with [*J*(P_AH) + *J*(P_BH)] equal to 9.0 Hz, a result that is quite comparable to that reported for *trans*-M(CO)₄(Tdp)₂ complexes (Tdp = tris-(dimethylamino)phosphine).²⁵ In a result that appears to be the norm for group 6B metal carbonyls, the ³¹P resonance shift for the *trans* isomer of Cr(CO)₄(DMPH)₂ is much further downfield than that for the *cis*.¹⁸

Properties exhibited by the M(CO)₄(DPH) compounds are completely consistent with the previous discussion. The $\nu(\text{CO})$ stretching frequencies are close to those for M(CO)₄(diphos), the hydrazine methyl resonance appears as a singlet upfield from the free ligand, and the ³¹P resonance values are in the order Cr > Mo > W. Evidence substantiating the chelated structure for the M(CO)₄(TMPH) species may be enumerated in the following manner: (1) elemental analyses and molecular weight determinations are consistent with the indicated monomeric formula, (2) the four $\nu(\text{CO})$ stretching frequencies are more comparable to tetracarbonyl derivatives containing

Table III. NMR Spectral Data of Phosphinohydrazine Metal Carbonyls and Related Derivatives

Compd	Proton NMR (J , Hz) ^a			³¹ Pb
	τ (NH)	τ (CH ₃)	τ (C ₆ H ₅)	
DMPH	6.81 (d, 11.0)	7.61 (s)	2.57 (m)	37.5
TMPH		7.47 (s), ^c 7.48 (d, 4.0) ^d	2.58 (m)	45.0
DPH		7.50 (s)	2.57 (m)	45.9
Cr(CO) ₅ (DMPH)	6.84 (d, 27.5)	7.78 (s)	2.35 (m)	100.4
Mo(CO) ₅ (DMPH)	6.84 (d, 26.5)	7.73 (s)	2.35 (m)	80.9
W(CO) ₅ (DMPH)	6.81 (d, 27.0)	7.77 (s)	2.37 (m)	64.2
Cr(CO) ₅ (DPH)		7.59 (d, 11.5)	2.43 (m)	
Mo(CO) ₅ (DPH)		7.59 (d, 11.5)	2.43 (m)	
Cr(CO) ₅ (TMPH)		7.51 (s), ^c 7.61 (d, 6.0) ^d	2.42 (m)	120.5
Mo(CO) ₅ (TMPH)		7.53 (s), ^c 7.63 (d, 6.0) ^d	2.48 (m)	101.2
W(CO) ₅ (TMPH)		7.50 (s), ^c 7.59 (d, 6.0) ^d	2.35 (m)	85.0
<i>trans</i> -Cr(CO) ₄ (DMPH) ₂	6.85 (d, 32.0)	7.83 (s)	2.40 (m)	114.9
<i>trans</i> -Cr(CO) ₄ (TMPH) ₂		7.62 (s), ^c 7.61 (t, 9.0) ^{d,e}	2.40 (m)	
<i>trans</i> -Mo(CO) ₄ (TMPH) ₂		7.63 (s), ^c 7.59 (t, 9.0) ^{d,e}	2.48 (m)	
<i>trans</i> -W(CO) ₄ (TMPH) ₂		7.63 (s), ^c 7.57 (t, 9.0) ^{d,e}	2.45 (m)	
<i>cis</i> -Cr(CO) ₄ (DMPH) ₂	6.85 (d, 32.0)	7.93 (s)	2.40 (m)	100.5
<i>cis</i> -Mo(CO) ₄ (DMPH) ₂	6.72 (d, 34.0)	7.90 (s)	2.42 (m)	81.6
<i>cis</i> -W(CO) ₄ (DMPH) ₂	6.68 (d, 33.0)	7.90 (s)	2.38 (m)	63.7
Cr(CO) ₄ (DPH)		7.60 (s)	2.42 (m)	124.7
Mo(CO) ₄ (DPH)		7.65 (s)	2.28 (m)	102.7
W(CO) ₄ (DPH)		7.63 (s)	2.29 (m)	81.9
Cr(CO) ₄ (TMPH)		7.17 (s), ^c 7.47 (d, 5.0) ^d	2.40 (m)	
Mo(CO) ₄ (TMPH)		7.07 (s), ^c 7.45 (d, 5.0) ^d	2.40 (m)	
W(CO) ₄ (TMPH)		6.87 (s), ^c 7.50 (d, 5.0) ^d	2.42 (m)	
Mo(CO) ₃ (DMPH) ₃	5.62 (d, 30.0)	7.78 (s)	2.65 (m)	
W(CO) ₃ (DMPH) ₃	5.55 (d, 29.0)	7.75 (s)	2.65 (m)	
W(CO) ₃ (TMPH) ₂		7.65 (m)	2.61 (m)	

^a Run in chloroform-*d* solutions with TMS internal standard; key to intensities: s = singlet, d = doublet, t = triplet, m = multiplet. ^b Ppm downfield from 85% H₃PO₄ external standard; run in methylene chloride solutions. ^c Protons in N(CH₃)₂. ^d Protons in N(CH₃). ^e Separation of the equally intense outer lines of the "triplet".

a phosphine and an amine group than two phosphines or two amines located in *cis* positions, (3) the phenyl proton resonance is depressed from free ligand values, (4) the N-methyl protons appear as the expected doublet, and (5) the N-dimethyl protons suffer a large downfield shift indicative of terminal nitrogen to metal bond formation.

Some rather unusual features were displayed by both varieties of molybdenum and tungsten phosphinohydrazine tricarbonyl derivatives isolated. Characteristic of C_{3v} *cis*-M(CO)₃(L)₃ geometry, the M(CO)₃(DMPH)₃ molecules exhibited two ν (CO) stretching bands in positions almost identical with those observed for a trisphosphine tricarbonyl compound. Although τ (CH₃) and J (³¹P-N-H) are in line with those recorded for other complexes in this study, ν (NH) occurs virtually unshifted from the free ligand value, τ (NH) is shifted far downfield from that observed for any other derivative, and τ (C₆H₅) is deshielded relative to the free ligand. Steric crowding is apparently contributing to this devious, spectral behavior in the more highly substituted tricarbonyls. A manifestation of the additional steric restrictions imposed by the N-methyl group in TMPH is the production of M(CO)₃(TMPH)₂ (M = Mo and W) instead of M(CO)₃(TMPH)₃ species. Comparison of the positions of the three ν (CO) bands with those of model compounds (Table II) suggests a molecule of C_s symmetry with one TMPH functioning as a monodentate ligand through the phosphorus atom and a second one chelating through the phosphorus and terminal nitrogen atoms. Similar to the DMPH tricarbonyls, the complex methyl and phenyl regions are centered upfield from the free ligand values.

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Registry No. Cr(CO)₅(DMPH), 52614-30-9; Mo(CO)₅(DMPH), 52614-31-0; W(CO)₅(DMPH), 52614-32-1; Cr(CO)₅(DPH), 56930-05-3; Mo(CO)₅(DPH), 56930-06-4; W(CO)₅(DPH),

56930-07-5; Cr(CO)₅(TMPH), 56930-08-6; Mo(CO)₅(TMPH), 56930-09-7; W(CO)₅(TMPH), 56930-10-0; *trans*-Cr(CO)₄(DMPH)₂, 56930-11-1; *trans*-Cr(CO)₄(TMPH)₂, 56930-12-2; *trans*-Mo(CO)₄(TMPH)₂, 56930-13-3; *trans*-W(CO)₄(DMPH)₂, 56930-14-4; *trans*-W(CO)₄(TMPH)₂, 56930-15-5; *cis*-Cr(CO)₄(DMPH)₂, 56994-00-4; *cis*-Mo(CO)₄(DMPH)₂, 56930-16-6; *cis*-W(CO)₄(DMPH)₂, 56994-01-5; Cr(CO)₄(DPH), 56930-17-7; Mo(CO)₄(DPH), 56930-18-8; W(CO)₄(DPH), 56930-19-9; Cr(CO)₄(TMPH), 56930-20-2; Mo(CO)₄(TMPH), 56930-21-3; W(CO)₄(TMPH), 56960-32-8; *cis*-Mo(CO)₃(DMPH)₃, 56930-22-4; *cis*-W(CO)₃(DMPH)₃, 56930-23-5; Mo(CO)₃(TMPH)₂, 56930-24-6; W(CO)₃(TMPH)₂, 56930-25-7; Mo(CO)₄(Nbd), 12146-37-1; Cr(CO)₄(Nbd), 12146-36-0; W(CO)₃(Cht), 12128-81-3; Mo(CO)₃(Cht), 12125-77-8.

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Cryoscopy in Acidic and Basic Aqueous Solvents. II. Eutectic Trifluoroacetic Acid¹

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Freezing points of eutectic aqueous trifluoroacetic acid (CF₃COOH, 10.6 mol %) and of solutions of ten ionic solutes in this solvent were determined from cooling curves. It was found that the molal freezing point depression was constant (within the experimental error) in all solutions (except nitric acid), with no noticeable dependence on the type of the ionic solute or its concentration. The average K_f was $6.53 \pm 0.01^\circ$. Solutions of nitric acid had a formal freezing point depression of $3.34 \pm 0.05^\circ$. This result confirmed conclusions of an earlier study on the dimerization of this acid in aqueous perchloric acid solutions.

Introduction

The precision of cryoscopic determinations of molecular weights of ionic species is greatly improved through the replacement of water by an aqueous electrolyte solution at its eutectic composition or at any other composition having a definite transition point. The lowering of the freezing point of such a solution is given by²

$$\lim_{m \rightarrow 0} \frac{\Delta T}{m} = \nu \frac{RT^{02}}{\lambda} = \nu K_f^0 \quad (1)$$

where ΔT is the lowering of the freezing temperature T^0 of the pure solvent, K_f^0 is the cryoscopic constant, m is the molality of the solute, λ is the specific (latent) heat of fusion of the pure solvent, and ν is the number of "foreign" particles produced per molecule (formula) of solute, e.g., $\nu = 1/2$ for dimerization and $\nu = 2$ for dissociation into two "foreign" species. "Foreign" species are those solute species which are not components of the pure solvent system. With one exception,¹ all solvent systems used were aqueous solutions of salts,³⁻⁵ hence the term "Salzkryoskopie". The classical and most widely used solvent of Salzkryoskopie is the saturated solution of Na₂SO₄ in water at the transition temperature of the decahydrate to the anhydrous salt (32.382°C). The transition temperature is depressed by "foreign" cations or anions but is not affected by ions common to the solvent and solute (i.e., Na⁺ or SO₄²⁻) in accordance with (1). This characteristic relation improves the precision of Salzkryoskopie as compared to ordinary water cryoscopy, since the relative change in ΔT caused by polymerization of an ion is much greater in the former.¹

The main drawback of Salzkryoskopie was its being restricted to solute species existing in neutral solutions (pH ~7). Many acidic solutes such as most transition metal aquoions are precipitated in neutral solutions and form stable solutions only in acidic media. Corrections for the acid added to stabilize such species were applied to cryoscopic data of Salzkryoskopie in order to overcome this difficulty,⁶ but the error introduced by the additional "foreign" ions (H⁺ and HSO₄⁻) increased rapidly with acid concentration and eventually wiped out the relative advantage of Salzkryoskopie over ordinary water cryoscopy. Some unwarranted conclusions were drawn from cryoscopic measurements in such systems.^{6,7}

In order to meet the specific requirements of acidic species, Ardon, Linenberg, and Halicz^{1,8} introduced the use of a

strongly acidic solvent, eutectic aqueous perchloric acid (40.75% HClO₄), and demonstrated its suitability for cryoscopic measurements with many mononuclear species as well as with binuclear ionic species^{1,7,8} such as Cr₂(OH)₂⁴⁺ and Mo₂O₄²⁺. Cryoscopic measurements of dilute solutions of nitric acid ($m \sim 0.02$) in this solvent revealed that this species exists as dimers in the perchloric acid solvent.^{1,9} In view of this surprising yet conclusive evidence it seemed desirable to check whether dimerization of dilute HNO₃ solution is confined to this solvent and temperature (-60°) or is a more general phenomenon, taking place in other acidic aqueous solvents and at higher temperatures. The purpose of the present work was to extend the scope of cryoscopy in acidic solutions by introducing a new acidic aqueous solvent and investigating its freezing-point depression by "normal" cationic and anionic species and by nitric acid. The solvent chosen was aqueous trifluoroacetic acid. This system had been reported¹⁰ as having a eutectic point at -21.55°C at a composition of 10.59 mol % CF₃COOH. The solid phases in equilibrium with the liquid are CF₃COOH·4H₂O + ice.

Experimental Section

The eutectic solvent was prepared by dilution of an appropriate weight of pure trifluoroacetic acid with water. The solutions of Zn(II), Mg(II), and Fe(II) in HTFAC were prepared by dissolving weighed samples of each metal in the eutectic acid. Solutions of H₂SO₄, HNO₃, and HClO₄ were prepared by dissolving the appropriate weights of their concentrated solutions in eutectic HTFAC. The solution of Fe(III) was prepared by dissolving freshly precipitated Fe(OH)₃ in the solvent. Solutions of Cr(III) and Th(IV) were prepared by absorption of solutions of their nitrates in HCl 0.1 N on cation exchange columns (Dowex 50WX2) and elution with eutectic HTFAC. The HCl solution was prepared by passing dry HCl gas through the eutectic solvent. Standard analytical methods were used to determine the concentration of each solute. The concentrations were adjusted to those given in Table I by dilution with eutectic HTFAC. Small quantities of water were added to some solutions in the process of their preparation (e.g., by neutralization of ferric hydroxide). No correction was made for this change in solvent composition since the eutectic temperature is not affected at all by this change and the increase of solute concentration at the freezing point is always less than 1%.

Freezing-point determinations were carried out in a double-walled Pyrex cell placed in a thermostated cooling bath which was maintained at $-27.00 \pm 0.02^\circ\text{C}$. The solution in the cell was stirred with a Pyrex stirrer at a constant rate of 100 rpm. The constancy of the cooling bath temperature and of the rate of stirring resulted in a constant rate of cooling of all solutions which, in turn, produced cooling curves of constant and equal slope in all measurements. This experimental