ture independence of the susceptibility that the present sample does not contain an impurity with unpaired spins. Since small amounts of spin-paired impurities would have no appreciable effect on the measured susceptibility, our result may be taken to be the susceptibility of the two nickel atoms in $[Ni\{P(C_6H_5)_2\}(CO)_2]_2$.

We conclude that the small paramagnetism of $[Ni\{P(C_6H_5)_2\}(CO)_2]_2$ is due entirely to the magnetic field mixing a high-lying excited state into the ground state. The spins of the two odd electrons are completely coupled at room temperature and are presumed to be paired in a Ni–Ni bond which is much stronger than the Cu–Cu bond in copper acetate. The possibility that the coupling takes place *via* orbitals on the bridging phosphorus atoms cannot, however, be excluded.

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Some Octamethyloxamidinium Salts of Metal Carbonyl Anions

BY R. B. KING

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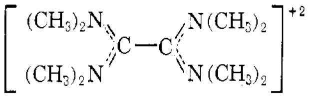
An important technique in preparative metal carbonyl chemistry is the use of alkali metals, generally as amalgams, for the reduction of various metal carbonyl derivatives to various metal carbonyl anions.[1] However, nonmetallic reducing agents[2,3] have never been reported as useful for the reduction of metal carbonyls to their corresponding anions.

Recently Wiberg and Buchler[4] have found tetrakis(dimethylamino)ethylene, $C_{10}H_{24}N_4$, to be a powerful two-electron reducing agent forming salts of the octamethyloxamidinium cation (I). Thus tetrakis(dimethylamino)ethylene reacts with halogens such as iodine to form the octamethyloxamidinium dihalides $[C_{10}H_{24}N_4]X_2$.



I

It has now been found that tetrakis(dimethylamino)ethylene reacts with certain metal carbonyl derivatives (Table I) to form octamethyloxamidinium salts of the corresponding metal carbonyl anions. The ionic nature of the products is indicated by the similarities of the infrared spectra in the metal carbonyl region (Table II) to those of other salts of the same metal carbonyl anions. Furthermore, the cobalt and vanadium derivatives were found to exhibit a high conductivity (Table I) in acetone solution.

The insolubility of the molybdenum derivative $[C_{10}H_{24}N_4][Mo(CO)_3C_5H_5]_2$ prevented measurement of its conductivity. Further evidence for the ionic nature of this insoluble material was provided by its reaction with benzyl chloride in tetrahydrofuran suspension to give $C_6H_5CH_2Mo(CO)_3C_5H_5$, m.p. 85–87°, in 7.2% conversion or 13.2% yield[5] after 66 hr.[6] The low yield and conversion in this reaction is probably a consequence of the insolubility of $[C_{10}H_{24}N_4][Mo(CO)_3C_5H_5]_2$. The other product in this reaction, water-soluble octamethyloxamidinium dichloride,[7] was detected by conversion to water-insoluble $[C_{10}H_{24}N_4][PF_6]_2$ by treatment with aqueous ammonium hexafluorophosphate. The $[C_{10}H_{24}N_4][PF_6]_2$, obtained in 14.5% conversion or 26.6% yield,[5] was identified by comparison of its infrared spectrum and melting point with those of authentic $[C_{10}H_{24}N_4][PF_6]_2$.[4]

Reactions of the carbonyls of cobalt and vanadium with tetrakis(dimethylamino)ethylene to give the corresponding metal carbonyl anion salts with the *metal-free* octamethyloxamidinium cation contrast with the reactions of these carbonyls with other amines where the corresponding metal carbonyl anion salts of the *metal-containing* ammine cations $[M^{II}(base)_6]^{2+}$ (M = Co or V; base = amine used for reaction) are produced.[1,8,9] This unique behavior clearly demonstrates the unusual ability for tetrakis(dimethylamino)ethylene to act toward metal carbonyl systems not as a Lewis base as other amines but instead as a two-electron reducing agent as noted by Wiberg and his coworkers for reactions with other systems.

π-Indenyltricarbonylmolybdenum dimer, $[C_9H_7Mo(CO)_3]_2$, is reduced by sodium amalgam[10] to give at least a 20% yield[11] of the anion $[C_9H_7Mo(CO)_3]^-$. Treatment of $[C_9H_7Mo(CO)_3]_2$ with tetrakis(dimethylamino)ethylene in tetrahydrofuran solution gives an

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[1] For a recent review of this chemistry see R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1965).

[2] The metal carbonyls themselves frequently effectively act as reducing agents when metal carbonyl anions are formed by their disproportionation, generally in the presence of Lewis bases.

[3] Organic reducing agents have been used in areas of transition metal chemistry other than metal carbonyls. See, for example, A. Davison, N. Edelstein, A. H. Maki, and R. H. Holm, *Inorg. Chem.*, **4**, 55 (1965), and references cited therein.

[4] N. Wiberg and J. W. Buchler, *Ber.*, **96**, 3223 (1963).

[5] This yield is based on unrecovered $[C_{10}H_{24}N_4][Mo(CO)_3C_5H_5]_2$.

[6] This product was identified by comparison of its infrared spectrum with that of authentic $C_6H_5CH_2Mo(CO)_3C_5H_5$, m.p. 88–89°, obtained from $NaMo(CO)_3C_5H_5$ and benzyl chloride (R. B. King and A. Fronzaglia, unpublished results).

[7] In complete contrast to the very water-soluble $[C_{10}H_{24}N_4]Cl_2$, $[C_{10}H_{24}N_4][Mo(CO)_3C_5H_5]_2$ appears to be completely insoluble in water.

[8] H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 2717 (1953); W. Hieber, W. Abeck, and J. Sedlmeier, *Angew. Chem.*, **64**, 480 (1952); *Ber.*, **86**, 705 (1953); W. Hieber, J. Sedlmeier, and W. Abeck, *ibid.*, **86**, 700 (1953); **87**, 25 (1954); I. Wender, H. W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, **74**, 1216 (1952).

[9] W. Hieber, J. Peterhans, and E. Winter, *Ber.*, **94**, 2572 (1961); W. Hieber, E. Winter, and E. Schubert, *ibid.*, **95**, 3070 (1962).

[10] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 475 (1965).

[11] This 20% yield of $[C_9H_7Mo(CO)_3]^-$ from $[C_9H_7Mo(CO)_3]_2$ and sodium amalgam is actually a minimum since this represents the maximum yield based on $[C_9H_7Mo(CO)_3]_2$ of $RMo(CO)_nC_9H_7$ compounds (R = methyl, $n = 3$; R = π-allyl, $n = 2$) obtained after treatment of the $[C_9H_7Mo(CO)_3]^-$ solution with the organic halide.

TABLE I

OCTAMETHYLOXAMIDINIUM SALTS FROM TETRAKIS(DIMETHYLAMINO)ETHYLENE AND METAL CARBONYL DERIVATIVES

Compound	Preparation	Solvent	Yield, %	Color		Molar conductance,[a] ohms^{-1} cm.^{2} mole^{-1}		Analyses,[b] %				
				Solid	Acetone soln.			C	H	N	O	Metal
$[C_{10}H_{24}N_4][Co(CO)_4]_2$	$C_{10}H_{24}N_4$[c] + $Co_2(CO)_8$	1:10 toluene–benzene	57	Orange[d]	Yellow	200–240	Calcd.	39.9	4.4	10.3	23.6	21.8
							Found	39.4	4.3	10.4	23.8	21.6
$[C_{10}H_{24}N_4][V(CO)_6]_2$[e]	$C_{10}H_{24}N_4$[c] + solvated $HV(CO)_6$[g]	Diethyl ether	23	Purple-brown	Yellow	320–365	Calcd.	41.4	3.8	8.8	30.1	16.0
							Found	39.9	3.8	8.8	30.9	16.0
$[C_{10}H_{24}N_4][Mo(CO)_3C_5H_5]_2$[f,h]	$C_{10}H_{24}N_4$[c] + $[C_5H_5Mo(CO)_3]_2$	Tetrahydrofuran or benzene	100	Orange-brown	Insol.	*i*	Calcd.	45.2	4.9	8.1	13.9	27.8
							Found	43.3	4.5	7.7	15.1	29.4
$[C_{10}H_{24}N_4][W(CO)_3C_5H_5]_2$[h]	$C_{10}H_{24}N_4$[c] + $C_5H_5W(CO)_3H$	Tetrahydrofuran	44	Brick-red	Insol.	*i*	Calcd.	36.0	3.9	6.4	11.1	
							Found	33.5	4.1	6.1	12.7	

[a] The molar conductance values given here were obtained in 0.0001 to 0.0006 *M* acetone solutions. [b] The analyses quoted here were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. [c] $C_{10}H_{24}N_4$ = tetrakis(dimethylamino)ethylene. This material, an air-sensitive liquid, was purchased from Chemical Intermediates and Research Laboratories, Cuyahoga Falls, Ohio. [d] Unlike the other compounds listed in this table $[C_{10}H_{24}N_4][Co(CO)_4]_2$ was air-sensitive in the solid state. The orange solid turned blue-violet over a period of hours. [e] This compound was also obtained as an immediate brown precipitate upon mixing aqueous solutions of octamethyloxamidinium bromide and $[Na(diglyme)_2][V(CO)_6]$. [f] This compound was also obtained as an immediate orange precipitate upon mixing aqueous solutions of octamethyloxamidinium bromide and $NaMo(CO)_3C_5H_5$. [g] The "$HV(CO)_6$" was obtained as a yellow $(C_2H_5)_2O$ solution by ether extraction of the mixture obtained from $[Na(diglyme)_2][V(CO)_6]$ and excess aqueous 3 *N* hydrochloric acid. [h] $[C_{10}H_{24}N_4][Mo(CO)_3C_5H_5]_2$: m.p. 171–173° dec. $[C_{10}H_{24}N_4][W(CO)_3C_5H_5]_2$: m.p. 152–153° dec. The other two compounds did not exhibit definite melting points. [i] The insolubility of these compounds in acetone prevented conductivity measurements.

TABLE II

INFRARED SPECTRA OF OCTAMETHYLOXAMIDINIUM SALTS[a] (CM.$^{-1}$)

Compound	ν_{CH}	ν_{CO}[b]	ν_{CN}[c]	Other bands
$[C_{10}H_{24}N_4][Co(CO)_4]_2$	2875 vw	1880 s, br[d]	1640–1620 br, s	1460 w, 1440 w, 1395 m, 1250 w, 1195 vw, 1165 vw, 1135 vw, 1090 vw, 1046 w, 874 w, 864 vw
$[C_{10}H_{24}N_4][V(CO)_6]_2$	*e*	1837 vs, br[f]	1653 m, 1640 sh	1443 w, 1410 w, 1400 sh, 1393 w, 1250 w, 1197 vw, 1169 w, 1132 vw, 1094 vw, 1050 w, 1008 vw, 877 w, 867 m, 847 vw
$[C_{10}H_{24}N_4][Mo(CO)_3C_5H_5]_2$	*e*	2046 m,[g] 1966 m,[g] 1958 m,[g] 1916 m,[g] 1888 s, 1767 s, 1745 s[h]	1659 m	1460 w, 1443 w, 1411 w, 1394 m, 1251 w, 1198 vw, 1171 vw, 1138 vw, 1100 vw, 1050 w, 1010 vw, 993 vw, 879 w, 866 w, 832 vw, 792 w, 783 w
$[C_{10}H_{24}N_4][W(CO)_3C_5H_5]_2$	*e*	2041 m,[g] 1966 m,[g] 1958 m,[g] 1916 m,[g] 1888 s, 1767 s, 1745 s[h]	1645 m	1451 vw, 1438 vw, 1407 vw, 1390 w, 1250 vw, 1193 vw, 1170 vw, 1134 vw, 1094 vw, 1049 vw, 1006 vw, 990 vw, 878 w, 865 w, 832 vw, 798 vw

[a] The metal carbonyl regions (1700 to 2100 cm.$^{-1}$) of these infrared spectra were investigated in halocarbon oil mulls and recorded on a Beckman IR-9 spectrometer. The remaining regions of the infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. [b] Metal carbonyl stretching frequencies of anion. [c] Stretching frequencies of the carbon–nitrogen multiple bonds in the octamethyloxamidinium cation. [d] O. Vohler, *Ber.*, **91**, 1161 (1958), reports various salts of the $Co(CO)_4^-$ anion to have a single strong metal carbonyl band in the range 1878–1916 cm.$^{-1}$. [e] The carbon–hydrogen stretching frequencies were too weak to be unequivocally observed. [f] W. Hieber, J. Peterhans, and E. Winter, *Ber.*, **94**, 2572 (1961), in collaboration with W. Beck, report salts of the $V(CO)_6^-$ anion to exhibit a single strong metal carbonyl band around 1860 cm.$^{-1}$. [g] These bands of varying relative intensities in different samples probably arise from some $[C_5H_5M(CO)_3]_2$ (M = Mo or W) present as an impurity. [h] Unfortunately no reports of the infrared spectra of $[C_5H_5M(CO)_3]^-$ (M = Mo or W) salts could be found in the literature. R. D. Fischer, *Ber.*, **43**, 165 (1960), reports that the closely related chromium compound $NaCr(CO)_3C_5H_5$ exhibits strong metal carbonyl bands at 1876 and 1695 cm.$^{-1}$. The infrared spectrum of the tetraethylammonium salt $[(C_2H_5)_4N][Mo(CO)_3C_5H_5]$ observed under the same conditions as the spectra listed in this table exhibited metal carbonyl bands at 2053 (m), 1983 (s), 1939 (m), 1889 (s) 1782 (s), and 1748 (s) cm. $^{-1}$.

insoluble brown material clearly indicated by analyses and its infrared spectrum to contain only relatively minor quantities of the expected $[C_{10}H_{24}N_4][Mo(CO)_3C_9H_7]_2$.

Alkali metals generally as amalgams reduce $[C_5H_5Fe(CO)_2]_2$[12] and $[C_5H_5NiCO]_2$[13] to the corresponding anions, $[C_5H_5Fe(CO)_2]^-$ and $[C_5H_5NiCO]^-$, respectively, and degrade $[CH_3SFe(CO)_3]_2$ to a complex mixture containing $Fe_3(CO)_{11}^{2-}$.[14] However, benzene or tetrahydrofuran solutions of $[C_5H_5Fe(CO)_2]_2$, $[C_5H_5NiCO]_2$, or $[CH_3SFe(CO)_3]_2$ appeared completely inert toward tetrakis(dimethylamino)ethylene as indicated by lack of color change or precipitate formation. This indicates that tetrakis(dimethylamino)ethylene is

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[12] E. O. Fischer and R. Böttcher, *Z. Naturforsch.*, **10b**, 600 (1955); T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

[13] D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1752 (1964).

[14] W. Hieber and A. Zeidler, *Z. anorg. allgem. Chem.*, **329**, 92 (1964).

a weaker reducing agent at least toward metal carbonyl systems than the free alkali metals.

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Stereochemical Nonrigidity in PF_3Cl_2 and PF_3Br_2

BY W. MAHLER AND E. L. MUETTERTIES

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In two earlier papers[1,2] we described an intramolecular rearrangement of fluorine atoms in PF_3Cl_2. We have examined PF_3Cl_2 as well as PF_3Br_2 in more detail and with greater precision and can now characterize these two phosphoranes as stereochemically nonrigid molecules.

The F^{19} n.m.r. spectra of PF_3Cl_2 and PF_3Br_2 below $-120°$ reveal two fluorine atom environments in each molecule. (The geometry is probably a C_{2v} trigonal bipyramid.[1-3]) At room temperature, there is just one fluorine atom environment with chemical shifts and P–F coupling constants (Table I) of the weighted average of the low-temperature values. These data demonstrate that no molecular change (*e.g.*, dimerization) occurs as a function of temperature.

TABLE I

F^{19} N.M.R. PARAMETERS AND EXCHANGE DATA[a]

	PF_3Cl_2	PF_3Br_2
J_{PF_a}	1023	1141
J_{PF_e}	1085	1143
J_{FF}	142	124
δ_F	−144	−181
δ_{F_e}	−36	−43
$J_{PF(av)}$ 25°	1050	1130
$J_{PF(av)}$ calcd.	1044	1124
$\delta_{F(av)}$ 25°	−112	−135
$\delta_{F(av)}$ calcd.	−108	−135
Exchange activation energy	7.2	7.2
τ_F (−50°)	$\sim 10^{-1}$	$\sim 10^{-2}$

[a] J in c.p.s., δ in p.p.m. from CF_3COOH, ΔH_a in kcal./mole, τ in sec.

Line-width analysis[4] of the transition region where the high-temperature doublet is undergoing broadening (−70 to +20°) gives a value for the activation energy for the fluorine exchange process of 7.2 ± 0.5 kcal./mole for both PF_3Cl_2 and PF_3Br_2. Since P–F coupling is maintained in the temperature region where the fluorine atoms lose their positional identity, the exchange process cannot involve P–F bond breaking. There is no difference in the n.m.r. transition region between liquid PF_3Cl_2 and a 25% solution of PF_3Cl_2 in petroleum ether. This insensitivity of exchange rate strongly supports an intramolecular process. Since the petroleum ether does not inhibit the exchange, a radical dissociative process

$$PF_3Cl_2 \rightleftharpoons PF_3Cl\cdot + Cl\cdot$$

is excluded. In addition, mixed solutions of PF_3Cl_2 and PF_3Br_2 display the sum of the individual, characteristic n.m.r. patterns at 20°. Since the two halides maintain their integrity, the possibility of the other dissociative process

$$PF_3X_2 \rightleftharpoons PF_3 + X_2$$

is eliminated.

The above observations establish a low-energy intramolecular fluorine exchange for PF_3Cl_2 and PF_3Br_2. Exchange through vibrational excitation is the only plausible process.[1,2,5,6] Since the exchange barriers are identical for PF_3Cl_2 and PF_3Br_2, the barrier must largely reflect anharmonic motion of the fluorine atoms.

[1] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

[2] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

[3] R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson, *ibid.*, **3**, 1748 (1964).

[4] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 222.

[5] S. Berry, *J. Chem. Phys.*, **32**, 933 (1960), discusses exchange in PF_5.

[6] E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

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Quadrupole Coupling in Boron Cage Compounds

BY D. R. EATON

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Recently a number of boron hydrides and their derivatives have been shown to possess cage structures. The electronic structure of these compounds presents a problem of some interest. The B^{11} quadrupole coupling constants constitute a relevant piece of information since such constants are proportional to the electric field gradient at the boron nucleus and therefore serve as a probe for the electron distribution. The magnitudes of these quadrupole coupling constants are accessible from n.m.r. experiments rather than by means of pure quadrupole resonance.[1] It is, in fact, in favorable cases, possible to obtain estimates of these parameters from the broad-line n.m.r. spectra of powdered, polycrystalline samples.[2-5] Application of this method

[1] M. H. Cohen and F. Reif, *Solid State Phys.*, **5**, 322 (1957).

[2] A. H. Silver and P. J. Bray, *J. Chem. Phys.*, **29**, 984 (1958).

[3] A. H. Silver and P. J. Bray, *ibid.*, **31**, 247 (1959).

[4] A. H. Silver and P. J. Bray, *ibid.*, **32**, 288 (1960).

[5] A. H. Silver and T. Kushido, *ibid.*, **38**, 865 (1963).