of 137.0 by vapor density (137.01 theoretical for CF_3ONF_2). *Anal.* Calcd. for CF_3ONF_2: F, 69.3; N, 10.2. Found: F, 71.7; N, 10.4. Vapor pressure measurements indicate a molar heat of vaporization of 4.4 kcal. and an extrapolated boiling point of 213.4°K. Experimental vapor pressure data are as follows (T (°K.), P (mm.)): 167.7, 45.0; 179.2, 103.0; 183.2, 131.8; 188.1, 187.6; 196.2, 297.2; 206.2, 523.; 210.2, 640. Between 167.7 and 210.2°K., the equation log $P_{\text{mm}} = 7.375 - 968.6T^{-1}$ may be used to calculate vapor pressures. The Trouton constant is 20.8.

A typical nuclear magnetic resonance spectrum is obtained with a broad triplet attributed to NF_2 ($\delta_{\text{CFCl}} = -124$ p.p.m., $J_{\text{N-F}} = 117$ c.p.s.) and a triplet to CF_3 ($\delta_{\text{CFCl}_3} = 63.0$ p.p.m., $J_{\text{NF-CF}} = 3.37$ c.p.s.). The relative peak areas are 2.0:3.0 (N–F:C–F). Positive ions observed in the mass spectrum, which was obtained with an ionizing voltage of 70 volts, listed in order of decreasing relative abundance include: CF_3^+, NF_2^+, NO^+, FCO^+, NF^+, F_2CO^+, CO^+ (or CO^+ and N_2^+), CF^+, CF_2^+. $NF_2OCF_2^+$, $NOCF_3^+$, NFO^+, and others were present in very low abundance.

The infrared spectrum obtained at 10 mm. pressure in a 5-cm. cell with sodium chloride windows consists of bands at 1302 (vs), 1240 (vs), 1218 (vs), 1026 (m), 940 (m), 890–910 (m), 869 (vs), and 715 (center of triplet) (m) cm.$^{-1}$.

The compound is stable in Pyrex glass either neat or in the presence of $CFCl_3$ at room temperature for several months. No decomposition is observed when it is held at 95° for 12 hr. However, decomposition was noted in Pyrex at 135–140° to give CF_4, NO_2, and SiF_4.

Acknowledgment.—This work was performed in part under contract with the Office of Naval Research and in part under a grant in aid from the Allied Chemical Co. (L. C. D.). Mr. B. J. Nist determined the n.m.r. spectrum.

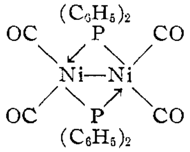
CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES,
INC., MURRAY HILL, NEW JERSEY 07971

Temperature Dependence of the Magnetic Susceptibility of Di-μ-(diphenylphosphido)bis(dicarbonylnickel)

BY A. P. GINSBERG AND E. KOUBEK

Received May 24, 1965

Hayter[1] has recently characterized a binuclear phosphorus-bridged complex of nickel(I) which he formulates with a metal–metal bond as



The infrared spectrum is consistent with either tetrahedral or *cis* planar geometry about the nickel atom. Room-temperature magnetic susceptibility measurements[1] gave for the corrected molar susceptibility $\chi'_{\text{M}} = +427 \times 10^{-6}$ c.g.s./mole. This small paramagnetism could be a temperature-independent susceptibility due to the magnetic field mixing a high-lying excited state into the ground state. On the other hand, the paramagnetism could result from the Ni–Ni bond being very weak, so that there is a thermally accessible triplet state which is appreciably occupied at room temperature. If this is so the susceptibility of $[Ni\{P(C_6H_5)_2\}(CO)_2]_2$ will exhibit a temperature dependence like that of copper acetate.[2] Finally, it may be that the paramagnetism is a consequence of the presence of a small amount of impurity with unpaired spins. If this is the case the susceptibility should follow a Curie or Curie–Weiss law.

In order to distinguish between the above three possibilities we have measured the magnetic susceptibility of $[Ni\{P(C_6H_5)_2\}(CO)_2]_2$ as a function of temperature between 298 and 120°K. The results are reported in this note.

Experimental

A sample of $[Ni\{P(C_6H_5)_2\}(CO)_2]_2$, sealed under nitrogen in a glass ampoule, was sent to us by Dr. Hayter. The sample was transferred (drybox) to a Teflon capsule which was then sealed with an air-tight closure. The susceptibility measurements were made in the standard way on a pendulum magnetometer[3] using a field of 14,200 oersteds.

Results and Discussion

The corrected[4] molar susceptibilities at twelve temperatures are given in Table I. It is clear that over the range studied the susceptibility is independent of temperature. The mean of the results in the table is $\chi'_{\text{M}} = 274 \pm 11 \times 10^{-6}$ c.g.s./mole. This is 35% less than the value reported for the room-temperature susceptibility. Hayter[1] has indicated that the sample used for the room-temperature measurement may have contained small amounts of Ni(II) due to surface oxidation of the crystals. This may explain the discrepancy. At any rate, it is evident from the tempera-

TABLE I
MAGNETIC SUSCEPTIBILITY OF $[Ni\{P(C_6H_5)_2\}(CO)_2]_2$

T, °K.	$10^6\chi'_{\text{M}}$, c.g.s./mole	T, °K.	$10^6\chi'_{\text{M}}$, c.g.s./mole
297	275	200	300
280	243	180	275
270	275	160	262
260	269	140	256
240	281	130	281
220	294	120	275

---

(1) R. G. Hayter, *Inorg. Chem.*, **3**, 711 (1964).

(2) See, for example, B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

(3) R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.*, **103**, 572 (1956).

(4) Diamagnetic correction = -275×10^{-6}. Calculated from the corrections given in P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, New York, N. Y., 1956. The diamagnetic correction for Ni(I) was taken to be -15×10^{-6}.

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.

Acknowledgment.—We thank Dr. Roy Hayter for the sample and H. J. Williams for allowing us to use his pendulum magnetometer.

CONTRIBUTION FROM THE MELLON INSTITUTE,
PITTSBURGH, PENNSYLVANIA

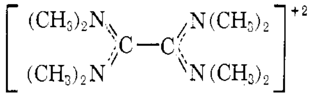
Some Octamethyloxamidinium Salts of Metal Carbonyl Anions

BY R. B. KING

Received May 14, 1965

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(di-



I

methylamino)ethylene reacts with halogens such as iodine to form the octamethyloxamidinium dihalides $[C_{10}H_{24}N_4]X_2$.

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

---

[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.