Contribution from the Corporate Research Laboratories,
Exxon Research and Engineering Company, Linden, New Jersey 07036

Preparation and Characterization of Transition Metal Carbonyl Derivatives of Magnesium: Evidence for Direct Metal-Metal Bonding between Magnesium and a Transition Metal

G. B. McVICKER

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Several facile synthetic routes are reported for the preparation of a wide variety of transition metal carbonyl derivatives of magnesium. These synthetically useful compounds can be represented by the general formula $B_xMg(M)_2$. The variability of the number of Lewis bases (B) coordinated to the magnesium atom, leading to either four ($x = 2$) or six ($x = 4$) coordination, can be related to the nucleophilicity of the transition metal carbonyl anion. Six-coordinate magnesium complexes invariably possess carbonyl bridges ($Mg—O{\equiv}C—M$) which are readily characterized by the presence of extremely low infrared carbonyl stretching frequencies. Four-coordinate magnesium complexes, depending upon the nucleophilicity of the transition metal carbonyl anion, can possess either carbonyl bridges or a direct magnesium–transition metal bond. Complexes containing a magnesium–transition metal linkage exhibit solution and spectroscopic properties similar to those given by covalent heterometal metal–metal bonded compounds.

Introduction

Recently several communications have described the preparation and partial characterization of transition metal carbonyl derivatives of magnesium.[1,2] These complexes offer considerable potential in synthetic organometallic chemistry since in many cases the compounds exhibit good hydrocarbon solubilities. Burlitch and coworkers have determined the crystal structure of $(py)_4Mg(Mo(CO)_3C_5H_5)_2$.[2] The molecule exhibits essentially octahedral coordination about the magnesium atom and in this respect is very analogous to the bonding found in $MgBr_2{\cdot}4C_4H_8O$.[3] The equatorial positions are occupied by the four pyridine molecules and the axial positions are filled by the two $Mo(CO)_3C_5H_5$ groups. Each $Mo(CO)_3C_5H_5$ group is bonded to the central magnesium atom via the oxygen atom of a single carbonyl group. The presence of a bridging carbonyl between a main group metal and a transition metal is readily detected by the appearance of low energy infrared carbonyl bands. The bridging carbonyl bands are commonly found 100 cm^{-1} lower in energy than those exhibited by the corresponding transition metal carbonyl anions.[4–7] Such large frequency decreases are the result of a lowered bond order in the bridging carbonyl group.

The existence of a bridging carbonyl group between two metals of disparate electronegativities is likely to alter the chemical reactivity of the carbonyl group and may also affect the metallating ability of the transition metal carbonyl residue. Since transition metal carbonyl derivatives of magnesium possess in numerous cases bridging carbonyl groups, these systems were of interest to us in our studies of catalytic olefin hydroformylation and alcohol carbonylation. With these applications in mind, we have examined numerous transition metal carbonyl derivatives of magnesium in an effort to understand the factors governing the formation of bridging carbonyl groups. From these studies conditions have been found which do not favor the formation of bridging carbonyl groups but result instead in the production of complexes containing a direct metal–metal interaction between magnesium and certain transition metal carbonyl groups. The interrelationship between bridging and nonbridging carbonyl structures of transition metal carbonyl derivatives of magnesium forms the basis of the present paper.

Experimental Section

Materials. Since transition metal carbonyl derivatives of magnesium are air sensitive, all reactions and sample preparations were carried out in an inert atmosphere enclosure under dry nitrogen. Benzene, tetrahydrofuran, and *n*-pentane were distilled from lithium aluminum hydride; pyridine was distilled over barium oxide and *N,N,N',N'*-tetramethyl-1,2-ethylenediamine (TMEDA) was distilled over calcium hydride. All distillations were carried out under dry nitrogen. Deuterated solvents were dried over Linde 4A molecular sieves. Solvents used in preparing NMR and infrared samples were either degassed by a freeze–thaw technique or by bubbling dry nitrogen through the liquids for several hours. The commercial transition metal carbonyl complexes used in this study were routinely rinsed with *n*-pentane and vacuum dried (10^{-4} mm) prior to use.

Preparative Methods. I. $(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$ was prepared by the reductive cleavage of 5.0 g of $(Fe(CO)_2C_5H_5)_2$ (Strem Chemicals Inc.) with 60 g of a 1% magnesium amalgam in 75 ml of tetrahydrofuran (THF). The 1% magnesium amalgam was prepared by rapidly stirring 0.6 g of 200 mesh magnesium powder (Research Organic/Inorganic Chemical Corp.) into 60 g of mercury. After allowing the reduction to continue for 18 hr at room temperature, the crude reaction mixture was suction filtered through a medium porosity glass frit. The yellow-green filtrate was concentrated under reduced pressure to approximately 25 ml. Yellow $(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$ was precipitated by flooding the concentrated THF solution with *n*-pentane. The yellow solid was recrystallized twice from benzene and vacuum dried (10^{-4} mm). The yield was 6.6 g (90%). A proton NMR spectrum of the complex in benzene solution consists of a sharp singlet at τ 5.30 due to the C_5H_5 group and two multiplets centered at τ 6.09 and 8.56 attributed to the complexed THF molecules. The intensity ratio of the complexed THF signals to the C_5H_5 signal was found to be 1.66 (calcd, 1.60). The chemical analyses for $(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$ and for the other transition metal carbonyl derivatives of magnesium prepared in this study are presented in Table I.

II. Alternatively $(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$ was prepared by contacting 6.0 g of $C_5H_5Fe(CO)_2I$[8] dissolved in 75 ml of THF with 1.0 g of 200 mesh magnesium powder in a heavy wall reaction tube equipped with a stopcock. After a short induction period (2–3 min), the reaction became sufficiently exothermic to warm the solvent to its reflux point. The initial dark red solution quickly became dark yellow and the reaction was over in 15 to 20 min (monitored by infrared). The crude reaction mixture was concentrated with reduced pressure and filtered to remove the insoluble $MgI_2{\cdot}x$THF complex produced during the reaction. The filtrate was flooded with *n*-pentane to precipitate the crude product. The crude product was washed with a 50:50 mixture of *n*-pentane–ether to remove any unreacted $C_5H_5Fe(CO)_2I$. Two recrystallizations from benzene yielded a pure product. The yield was 4.95 g (96%).

III. $(C_5H_5N)_2Mg(Fe(CO)_2C_5H_5)_2$ was obtained by the reduction of 5.0 g of $(Fe(CO)_2C_5H_5)_2$ with 50 g of a 1% magnesium amalgam in a solution containing 125 ml of benzene and 6.7 g of pyridine. After allowing the reduction to continue for 18 hr at room temperature, the crude reaction was suction filtered. The filtrate was concentrated to approximately 40 ml with reduced pressure. The concentrate was flooded with *n*-pentane, knocking out of solution a bright yellow solid. The yellow solid was recrystallized from benzene and vacuum dried. The yield was 7.2 g (95%). A proton NMR spectrum of the complex in THF solution consists of a sharp singlet at τ 5.75 due to the C_5H_5 group and multiplets centered at τ 1.51, 2.46, and 2.80 due to pyridine.

Table I. Transition Metal Carbonyl Derivatives of Magnesium

	Analytical results											
	Calcd, %						Found, %					
Compd	C	H	Mg	M	P	N	C	H	Mg	M	P	N
$(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$	50.6	5.02	4.65	21.4			49.7	4.83	4.64	22.5		
$(C_5H_5N)_2Mg(Fe(CO)_2C_5H_5)_2$	53.7	3.76	4.53	20.8		5.22	54.9	5.16	4.82	17.7		5.76
$(C_4H_8O)_4Mg(Mo(CO)_2(PCH_3(C_6H_5)_2)C_5H_5)_2$	58.6	5.97	2.12	16.7	5.40		58.3	5.61	2.09	17.4	6.25	
$(C_4H_8O)_4Mg(Mo(CO)_2(P(C_4H_9)_3)C_5H_5)_2$	56.3	8.40	2.11	16.7	5.39		55.8	8.37	2.37	18.0	5.51	
$(C_5H_5N)_4Mg(Co(CO)_4)_2$	49.3	2.95	3.42	17.3		8.21	49.4	3.26	2.91	17.1		7.79
$(C_4H_8O)_4Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$	57.6	5.85	2.43	11.8	6.20		55.9	6.01	2.36	11.1	6.26	
$(C_5H_5N)_4Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$	60.8	4.51	2.37	11.5	6.03	5.46	58.6	4.51	2.51	11.7	5.69	5.41
$(C_6H_{16}N_2)_2Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$	56.0	6.20	2.58	12.5			53.5	6.14	2.66	12.9		
$(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9)_3))_2$	55.1	8.64	2.42	11.7	6.17		54.6	8.74	2.45	11.4	5.99	

The ratio of the pyridine signal intensities to the C_5H_5 signal intensity was found to be 0.96 (calcd, 1.0).

IV. $(C_4H_8O)_4Mg(Mo(CO)_3C_5H_5)_2$ was prepared either by the reduction of $(Mo(CO)_3C_5H_5)_2$ (Pressure Chemical Co.) or $C_5H_5Mo(CO)_3I$[8] with a twofold excess of a 1% magnesium amalgam in THF solution. The reaction product is an extremely air-sensitive off-white solid which is only sparingly soluble in organic solvents. Numerous chemical analyses for this compound were not satisfactory. A proton NMR spectrum of the complex in acetonitrile-*d* consists of a sharp singlet at τ 5.18 due to the C_5H_5 group and multiplets at τ 6.59 and 8.47 due to THF. In acetonitrile-*d* solution the complexed THF molecules are displaced by solvent. The NMR spectrum of the acetonitrile-*d* complex, however, allows one to establish the stoichiometry of the solid THF complex by comparing the free THF signals with the intensity of the C_5H_5 signal. This intensity ratio was found to be 3.20 (calcd, 3.20).

V. $(C_5H_5N)_4Mg(Mo(CO)_3C_5H_5)_2$ was obtained by a route similar to that outlined in preparation III. In acetonitrile-*d* solution the light green complex exhibits a sharp proton NMR singlet at τ 5.23 due to the C_5H_5 group and multiplets centered at τ 1.78, 2.42, and 2.84 arising from free pyridine. The intensity ratio of the free pyridine signals to the C_5H_5 signal was found to be 2.20 (calcd, 2.0).

VI. $(C_4H_8O)_4Mg(Mo(CO)_2(P(C_4H_9)_3)C_5H_5)_2$ was obtained by allowing a 200 ml THF solution containing 11.0 g of $C_5H_5Mo(CO)_2(P(C_4H_9)_3)I$[9] to react with 80 g of a 1% magnesium amalgam at room temperature for 18 hr. The crude reaction mixture was concentrated to 40 ml under reduced pressure and then filtered to remove the suspended $MgI_2{\cdot}x$THF reaction product. The clear yellow filtrate was reduced to near dryness and flooded with *n*-pentane which immediately caused the precipitation of a yellow solid. The solid was collected and rinsed several times with *n*-pentane and then vacuum dried. The yield was 9.3 g (81%). The proton NMR spectrum of the complex in benzene contains a sharp singlet at τ 4.64 due to the C_5H_5 group, a pair of multiplets at τ 5.91 and 8.22 due to complexed THF, and a multiplet centered near τ 8.6 due to the $P(C_4H_9)_3$ ligand. The $P(C_4H_9)_3$ to THF signal intensity ratio was found to be 1.82 (calcd, 1.69) and the $P(C_4H_9)_3$ to C_5H_5 signal intensity ratio was found to be 5.5 (calcd, 5.4).

VII. $(C_4H_8O)_4Mg(Mo(CO)_2(PCH_3(C_6H_5)_2)C_5H_5)_2$ was prepared in a manner similar to that given in preparation VI. A proton NMR spectrum of the yellow complex in benzene solution consists of a sharp singlet at τ 5.40 due to the C_5H_5 group, two multiplets at τ 6.83 and 9.15 due to the complexed THF molecules, and a doublet centered at τ 8.44 due to CH_3–P (J_{P-CH_3} = 7.0 Hz). The intensity ratio of the THF signals to the C_5H_5 signal was found to be 3.40 (calcd, 3.20) and the intensity ratio of the C_5H_5 signal to the P–CH_3 signals was found to be 1.66 (calcd, 1.67).

VIII. $(C_5H_5N)_4Mg(Co(CO)_4)_2$ was prepared by a route similar to that outlined in preparation III.

IX. $(C_4H_8O)_4Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$ was prepared by the reduction of $Co_2(CO)_6(PCH_3(C_6H_5)_2)_2$[10] with a twofold excess of a 1% magnesium amalgam in THF solution. A proton NMR spectrum of the yellow complex in acetone-*d* solution exhibited a multiplet centered at τ 3.08 assigned to P–C_6H_5, a pair of multiplets centered at τ 6.97 and 8.72 due to THF, and a doublet centered at τ 8.28 due to P–CH_3 (J_{P-CH_3} = 9 Hz). The intensity ratio of the THF signals to the P–C_6H_5 signal was found to be 1.5 (calcd 1.60). The position and chemical shift difference exhibited by the α and β protons of the THF molecules suggest that the originally complexed THF molecules are free in acetone-*d*, having been replaced with solvent molecules.

Table II. Molecular Weights

		Found	
Compd	Calcd	Benzene[a]	Tetrahydrofuran[b]
$(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$	522	528	542
$(C_5H_5N)_2Mg(Fe(CO)_2C_5H_5)_2$	536	496	
$(C_4H_8O)_4Mg(Mo(CO)_2(PCH_3(C_6H_5)_2))_2$	1147	433	
$(C_4H_8O)_4Mg(Mo(CO)_2(P(C_4H_9)_3)C_5H_5)_2$	1152	599	
$(C_5H_5N)_4Mg(Co(CO)_4)_2$	683	665	
$(C_5H_5N)_4Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$	1027	842	
$(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9)_3))_2$	1003	310	972

[a] Cryoscopic method. [b] Vapor pressure depression method.

X. $(C_5H_5N)_4Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$ was prepared by the reduction of $Co_2(CO)_6(PCH_3(C_6H_5)_2)_2$ with a twofold excess of a 1% magnesium amalgam in benzene solution to which was added a slight excess of pyridine.

XI. $(C_6H_{16}N_2)_2Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$ was obtained by reducing $Co_2(CO)_6(PCH_3(C_6H_5)_2)_2$ with a twofold excess of a 1% magnesium amalgam in the presence of a twofold excess of TMEDA. The proton NMR spectrum of the yellow chelated complex in acetonitrile-*d* exhibited a multiplet centered at τ 2.81 and 3.00 due to P–C_6H_5, a doublet at τ 8.45 due to P–CH_3 (J_{P-CH_3} = 5.5 Hz), and a complex multiplet exhibiting two major signals at τ 7.80 and 8.06 assigned to the complexed TMEDA molecule. The intensity ratios of the TMEDA signals to the P–C_6H_5 and P–CH_3 signals were found to be 1.68 and 5.18, respectively (calcd, 1.60 and 5.33).

XII. $(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9)_3))_2$ was prepared by the reduction of $Co_2(CO)_6(P(C_4H_9)_3)_2$[9] with a 1% magnesium amalgam in THF solution. The proton NMR spectrum of the yellow-green complex in benzene solution exhibited a multiplet centered near τ 8.5 due to $P(C_4H_9)_3$ and two multiplets centered at τ 6.03 and 8.45 due to THF. The intensity ratio of the $P(C_4H_9)_3$ multiplet to the THF signals was found to be 1.72 (calcd 1.69).

Microanalyses of the compounds prepared in this study (Table I) were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Equipment. Infrared spectra (Table III) were measured on either a Beckman Model 20 or a Perkin-Elmer Model 621 grating spectrometer. Solution measurements were made using matched 0.1 mm KBr liquid cells supplied by International Crystal Laboratories. Solid samples were measured as Nujol mulls between KBr plates. The infrared spectra were routinely calibrated with a polystyrene film.

NMR measurements were carried out with a Varian A-60 instrument employing torch sealed sample tubes. NMR samples were externally referenced with TMS.

Conductivity measurements were obtained with a conductivity bridge, Model PM-70CM, manufactured by the Barnstead Co. The conductivity probe, supplied by Industrial Instruments, was equipped with platinum electrodes having a cell constant of 1.0. The small size of the conductivity measuring apparatus allowed the experiments to be performed inside the drybox.

Molecular weights (Table II) in benzene solution were measured cryoscopically with an Advanced Instrument Inc. cyroscope. Sample solutions were protected with an argon atmosphere. Molecular weights in THF were obtained by the vapor pressure depression method employing an electronic pressure meter manufactured by MKS Instruments Inc.[11] The vapor pressure measurements were carried out at 0° using carefully degassed analytical samples.

Results and Discussion

General Properties of Transition Metal Carbonyl Derivatives of Magnesium. Transition metal carbonyl derivatives of magnesium can be prepared by several routes.[12] The most general method of preparation is the reductive cleavage of dimeric transition metal carbonyl complexes with a dilute magnesium amalgam in the presence of a Lewis base (B). A representative preparation is given by eq 1. The Lewis base

$$(Fe(CO)_2C_5H_5)_2 + Mg(Hg) \xrightarrow{B} B_xMg(Fe(CO)_2C_5H_5)_2 \qquad (1)$$

(such as THF, pyridine or TMEDA) can be supplied either by the solvent or by the addition of a slight excess of base to a hydrocarbon reduction medium. The reductive cleavage results in the nearly quantitative formation of bis transition metal carbonyl derivatives of magnesium.

A second preparative route involves the reduction of transition metal carbonyl halide complexes with either magnesium powder or a dilute magnesium amalgam. The reduction may proceed through a transition metal Grignard intermediate which rapidly disproportionates into a bis transition metal carbonyl derivative of magnesium and magnesium halide (eq 2 and 3) in the presence of a Lewis base.

$$C_5H_5Fe(CO)_2I + Mg(Hg) \xrightarrow{B} \text{“}C_5H_5Fe(CO)_2MgI{\cdot}xB\text{”} \qquad (2)$$

$$2(C_5H_5Fe(CO)_2MgI{\cdot}xB) \xrightarrow{B} B_xMg(Fe(CO)_2C_5H_5)_2 + B_xMgI_2 \qquad (3)$$

Transition metal carbonyl Grignard complexes have not been detected in solution even though Carrick and Glockling[13] and Burlitch and Ulmer[14] have suggested the stability of species of this type.

Transition metal carbonyl derivatives of magnesium, $B_xMg(M)_2$, can be isolated as crystalline solids but they must be handled with care as they are extremely sensitive to air. Upon air exposure the complexes are rapidly oxidized to MgO and the corresponding dimeric transition metal carbonyl complex:

$$B_xMg(M)_2 \xrightarrow{O_2} MgO + M\text{–}M + xB \qquad (4)$$

The Lewis bases are strongly complexed as the solid compounds remain unchanged after prolonged (24 hr) periods of time under a vacuum of 10^{-4} mm at room temperature. As a class the compounds are thermally stable, decomposing without melting at temperatures greater than 150°.

The organic solvent solubility of the $B_xMg(M)_2$ complexes is highly dependent upon the nature of the complexed Lewis base. The solubilities of the THF, pyridine, and TMEDA adducts in benzene generally follow the order THF < pyridine < TMEDA. The solubility of the complexes is greatly enhanced by substituting an organophosphine ligand for carbon monoxide in the transition metal carbonyl moiety. Alkyl substituted phosphines generally give higher hydrocarbon solubility than aryl phosphines.

As a result of their hydrocarbon solubility, $B_xMg(M)_2$ complexes are useful metallating agents. For example, $((C_6H_5)_3P)_3CuCo(CO)_3P(C_4H_9)_3$ was prepared by the metathetical reaction of $(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9)_3))_2$ with $((C_6H_5)_3P)_3CuCl$ in hexane solution. In a more conventional preparation employing $NaCo(CO)_3P(C_4H_9)_3$ in THF, only copper metal and $((C_6H_5)_3P)_2Cu(Co(CO)_3(P(C_4H_9)_3))_2$ were obtained, as the polar solvent assisted the disproportionation of the initially formed Cu(I) complex. Thus in cases where the failure to isolate mixed metal complexes can be attributed to solvent aided disproportionations, the use of hydrocarbon soluble, magnesium–transition metal carbonyl complexes appears very attractive.

For 0.05 *M* THF solutions the molar conductivities range from $\Lambda_M = 0.010$ for $(C_5H_5N)_2Mg(Fe(CO)_2C_5H_5)_2$ to $\Lambda_M = 0.18$ for $(C_5H_5N)_4Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$. These numbers when compared with $\Lambda_M = 12.4$ for a 0.05 *M* THF solution of $NaCo(CO)_4$[15] suggest that the magnesium derivatives are essentially nonionized in THF solution. This observation is substantiated by the absence in THF solutions of these complexes of infrared bands due to the well-known carbonyl anions.

In benzene solution the complexes $(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$, $(C_5H_5N)_2Mg(Fe(CO)_2C_5H_5)_2$, and $(C_5H_5N)_4Mg(Co(CO)_4)_2$ were found to exhibit monomeric molecular weights (Table II). The $(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$ complex was also found to be monomeric in THF solution. Tetrakis Lewis base adducts such as $(C_4H_8O)_4Mg(Mo(CO)_2(PCH_3(C_6H_5)_2)C_5H_5)_2$, $(C_5H_5N)_4Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$, and $(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9)_3))_2$ were in contrast found to exhibit molecular weights in benzene solution considerably lower than those predicted by stoichiometry. For example, $(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9)_3))_2$ was found to give an apparent molecular weight of 310 (calcd, 1003). The absence of ionization in benzene solution suggests that dissociation arises by the loss of two molecules of Lewis base from the complex producing thereby a tetrahedrally coordinated magnesium complex (eq 5). In THF solution the

$$(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9))_2 \rightleftharpoons (C_4H_8O)_2Mg(Co(CO)_3(P(C_4H_9)_3))_2 + 2C_4H_8O \qquad (5)$$

complex exhibits a normal molecular weight which suggests that magnesium retains octahedral coordination in the polar ether solvent. In benzene solution the dissociation of an analogous tetrakis pyridine adduct, $(C_5H_5N)_4Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$, is not as extensive as the tetrakis THF adduct. This suggests that pyridine is more tightly bound to the magnesium atom. The high degree of dissociation found in benzene solutions of $(C_4H_8O)_4Mg(Mo(CO)_2(PCH_3(C_6H_5)_2)C_5H_5)_2$ by molecular weight measurements (found, 433; calcd, 1147) has been substantiated by NMR. In the NMR study a sealed sample of the tetrakis THF adduct in benzene solution was found to slowly precipitate a yellow solid. After 72 hr only NMR signals due to free THF were observed with integrated intensities corresponding to one-half the original THF signal. When taken up in acetone-*d*, the benzene insoluble yellow solid yielded an NMR spectrum consistent with a bis THF adduct. The starting tetrakis THF adduct can be regenerated by dissolving the bis THF adduct in THF and precipitating with *n*-pentane. Molecular weight measurements of $(C_4H_8O)_4Mg(Mo(CO)_2(P(C_4H_9)_3)C_5H_5)_2$ in benzene indicate that this complex also undergoes considerable dissociation in solution (found, 599; calcd, 1152). This complex, in contrast to the $PCH_3(C_6H_5)_2$ substituted complex, does not precipitate a lower THF solvate upon standing in benzene solution.

The number of Lewis bases found complexed to solid transition metal carbonyl derivatives of magnesium correlates well with the nucleophilicity of the transition metal carbonyl anion.[16] When M in $B_xMg(M)_2$ is strongly nucleophilic, such as $Fe(CO)_2C_5H_5^-$, complexes containing two molecules of Lewis base crystallize from solution. Less nucleophilic anions such as $Mo(CO)_2(L)C_5H_5^-$ and $Co(CO)_3L^-$ (L = CO or an organophosphine) yield solid derivatives containing four complexed Lewis bases. The tendency for tetrakis Lewis base adducts to dissociate in nonpolar solvents is also related to the nucleophilicity of the transition metal anion. For example, in benzene solution $(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9)_3))_2$ is more extensively dissociated than $(C_4H_8O)_4Mg(Mo(CO)_2(P(C_4H_9)_3)C_5H_5)_2$. This suggests that the more nucleophilic $Co(CO)_3P(C_4H_9)_3^-$ anion is better able to elec-

Table III. Infrared Bands in CO Stretching Region for Transition Metal Carbonyl Derivatives of Magnesium in Various Solvent Systems

Compd	Nujol mull	Benzene soln	Tetrahydrofuran soln
$(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$	2018 w	2015 w	2009 w
	1962 w	1921 vs	1959 w
	1925 vs	1854 vs	1918 s
	1854 vs		1884 vs
	1772 vs		1854 s
			1713 vs
$(C_5H_5N)_2Mg(Fe(CO)_2C_5H_5)_2$	2024 w	2018 w	
	1966 w	1917 vs	
	1921 sh	1847 vs	
	1905 vs		
	1834 vs		
$(C_4H_8O)_4Mg(Mo(CO)_3C_5H_5)_2$	1908 vs	1925 vs	1912 vs
	1810 vs	1825 vs	1815 vs
	1674 vs	1668 vs	1680 vs
$(C_5H_5N)_4Mg(Mo(CO)_3C_5H_5)_2$	1918 vs	1922 vs	
	1826 vs	1825 vs	
	1659 vs	1665 vs	
$(C_4H_8O)_4Mg(Mo(CO)_2(PCH_3(C_6H_5)_2)C_5H_5)_2$	1802 vs	1800 s	1817 vs
	1627 vs	1732 vs	1622 vs
		1617 vs	
$(C_4H_8O)_4Mg(Mo(CO)_2(P(C_4H_9)_3)C_5H_5)_2$	1788 vs, br	1791 vs	1796 vs
	1604 vs, br	1737 vs	1595 vs
		1702 s	
		1687 s	
		1624 s	
		1592 vs	
		1791 vs[a]	
		1594 vs[a]	
$(C_5H_5N)_4Mg(Co(CO)_4)_2$	2008 w	2016 w	
	1978 sh	1975 w	
	1925 vs, br	1939 vs	
	1785 vs	1764 vs	
$(C_4H_8O)_4Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$	1972 w	1970 w	1970 w
	1940 vs	1947 vs	1952 vs
	1868 vs	1891 vs	1886 vs
	1739 vs	1721 vs	1724 vs
$(C_5H_5N)_4Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$	1944 m-s	1950 m-s	1950 m-s
	1877 vs	1915 m-s	1885 vs
	1728 vs	1882 vs	1721 vs
		1712 vs	
$(C_6H_{16}N_2)_2Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$	1942 m-s	1965 s	1970 w, sh
	1862 vs	1895 s	1952 s
	1729 vs	1718 s	1886 vs
			1722 vs
$(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9)_3))_2$	1959 m	1952 w	1956 m
	1927 m-s	1925 w	1936 vs
	1853 vs	1896 vs	1866 vs
	1720 vs	1874 vs	1706 vs

[a] 10% THF/benzene.

tronically stabilize a tetrahedrally substituted magnesium complex in solution.

Infrared Studies of Transition Metal Carbonyl Derivatives of Magnesium. $B_2Mg(Fe(CO)_2C_5H_5)_2$ Complexes. Linear Fe–M–Fe complexes such as $Hg(Fe(CO)_2C_5H_5)_2$ and $Zn(Fe(CO)_2C_5H_5)_2$ exhibit three strong carbonyl stretching frequencies, 1944, 1969, and 1932 cm^{-1} and 1968, 1894, and 1867 cm^{-1}, respectively, for the mercury and zinc derivatives.[17,18] Angular complexes such as $I_2Sn(Fe(CO)_2C_5H_5)_2$[19] also give rise to three infrared active carbonyl bands (2026, 2002, 1974 cm^{-1}) while ionic $Fe(CO)_2C_5H_5^-$ compounds display two strong bands near 1860 and 1770 cm^{-1}.[20] The mercury, zinc, and tin derivatives exhibit one more infrared carbonyl band than predicted by the local symmetry of the $Fe(CO)_2C_5H_5$ group.[21] This is a consequence of vibrational coupling (via Fe–M–Fe) between the two $Fe(CO)_2C_5H_5$ moieties. In benzene solution, the monomeric $B_2Mg(Fe(CO)_2C_5H_5)_2$ (B = THF or pyridine) complexes exhibit two strong carbonyl bands near 1920 and 1850 cm^{-1} and a weak band near 2020 cm^{-1} (Table III). If it is assumed that the four substituents are tetrahedrally disposed about the magnesium atom, the resolution of two strong carbonyl bands is consistent with there being little interaction between the two $Fe(CO)_2C_5H_5$ groups (local symmetry obeyed). The carbonyl bands of the magnesium derivative are intermediate in energy between those found in covalent mercury and zinc complexes and the $Fe(CO)_2C_5H_5^-$ anion. Since the energies of carbonyl absorptions are shifted to lower frequencies as the electron density on the transition metal increases[22] (π-electron density donation from appropriate d orbitals on the metal to the antibonding orbital of the carbonyl group increases and thereby lowers the C–O bond order), the polarity of the magnesium–iron bond is somewhat greater than the mercury–iron or zinc–iron bonds but less than that of a purely ionic complex. In benzene solution the bis pyridine complex exhibits slightly lower carbonyl bands (4–7 cm^{-1}) than the bis THF adduct. Such shifts are consistent with pyridine being a better electron donor toward magnesium than THF.

The infrared spectrum of solid $(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$ is characterized by three strong carbonyl bands at 1925, 1854, and 1772 cm^{-1}. The 1772 cm^{-1} band most likely results from partial ionization in the solid state since this frequency is very close in energy to the low energy band exhibited by the $Fe(CO)_2C_5H_5^-$ anion. A band near 1770 cm^{-1}

is absent in the solid state infrared spectrum of $(C_5H_5N)_2Mg(Fe(CO)_2C_5H_5)_2$. This suggests that the pyridine adduct does not assume an ionic crystal lattice.

The complexity of the carbonyl region in the infrared spectrum of $(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$ in THF solution indicates the presence of several solution species. The spectrum can be satisfactorily accounted for by the following equilibrium (eq 6):

$$(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2 + 2C_4H_8O \rightleftharpoons (C_4H_8O)_4Mg(Fe(CO)_2C_5H_5)_2 \qquad (6)$$

The two strong bands situated at 1918 and 1854 cm^{-1} are assigned to a bis THF adduct since these same two frequencies are exhibited by benzene solutions of the well characterized bis THF complex. The two very strong bands at 1884 and 1713 cm^{-1} are assigned to a tetrakis THF adduct. Aged solutions show no measurable deviation in the relative concentration of the two species. The low frequency carbonyl band at 1713 cm^{-1} is very likely associated with a bridging carbonyl group ($\mathrm{Mg{-}O{\equiv}C{-}Fe}$) since it appears nearly 60 cm^{-1} lower in energy than the low frequency band of the $Fe(CO)_2C_5H_5^-$ anion. The changeover from a relatively covalent Mg–Fe interaction found for the bis THF adduct in benzene to a complex containing a $\mathrm{Mg{-}O{\equiv}C{-}Fe}$ interaction in THF solution is ascribed to the enhanced solvation of the magnesium atom in the polar ether solvent. The reported infrared spectrum of $(C_5H_5N)_4Mg(Fe(CO)_2C_5H_5)_2$ in pyridine solution[2] contains two strong carbonyl bands at 1875 and 1711 cm^{-1}. In this case the major solution species can be reasonably assumed to be a tetrakis pyridine adduct which contains bridging carbonyl groups in the axial positions.[2] The close agreement between the spectrum of the tetrakis pyridine adduct and the spectrum attributed to a tetrakis THF adduct gives credence to our assignment.

The reactivity of magnesium–iron carbonyl complexes was found to be solvent dependent. For example, the exchange reaction in benzene solution between $Hg(CN)_2$ and $(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$ is about 30% complete after 24 hr, but upon addition of a small amount of THF, the formation of $Hg(Fe(CO)_2C_5H_5)_2$ is complete in several minutes. This observation implies that the nucleophilicity of the $Fe(CO)_2C_5H_5$ group is markedly enhanced by polar solvents. The enhanced nucleophilicity is likely the result of a changeover from a covalent Mg–Fe bonded complex in benzene to a solvated ion pair in THF solution which possesses a polar ($\mathrm{Mg{-}O{\equiv}C{-}Fe}$) interaction.

$B_4Mg(Mo(CO)_2(L)C_5H_5)_2$ Complexes. The infrared spectra of complexes of the general formula $B_4Mg(Mo(CO)_2(L)C_5H_5)_2$ where B = THF or pyridine and L = CO, $P(C_4H_9)_3$, or $PCH_3(C_6H_5)_2$ are presented in Table III. In complexes where L = CO the tetrakis THF and pyridine adducts exhibit three strong carbonyl bands near 1910, 1820, and 1665 cm^{-1} in the solid state and in solution in benzene and THF. The locations of these frequencies are in good agreement with those reported for $(C_5H_5N)_4Mg(Mo(CO)_3C_5H_5)_2$.[2] The low energy band near 1665 cm^{-1}, some 80 cm^{-1} lower in frequency than that found in ionic derivatives[23] such as the tris ethylenediamine adduct of $Cd(Mo(CO)_3C_5H_5)_2$ (1888, 1778, 1744 cm^{-1}), is assigned to a bridging group ($\mathrm{Mg{-}O{\equiv}C{-}Mo}$) occupying an axial position in the six-coordinated magnesium complex.[2]

Several phosphine substituted $Mo(CO)_2(PR_3)C_5H_5$ derivatives of magnesium were prepared in an attempt to obtain magnesium–molybdenum carbonyl complexes devoid of bridging carbonyl groups. We reasoned that by replacing a CO group in $Mo(CO)_3C_5H_5$ with a better σ-donating and poorer π-accepting ligand such as an organophosphine the nucleophilicity of the molybdenum atom would be increased to the point where Mg–Mo bonded complexes similar to the above Mg–Fe bonded complexes might be produced. The infrared spectra of the $(C_4H_8O)_4Mg(Mo(CO)_2(L)C_5H_5)_2$ (L = $P(C_4H_9)_3$ or $PCH(C_6H_5)_2$) complexes in either the solid state or in THF solution are characterized by the presence of two strong carbonyl bands near 1800 and 1600 cm^{-1}. The resolution of two carbonyl bands in the solid state and THF solution spectra suggest that the two $Mo(CO)_2(L)C_5H_5$ groups are not vibrationally coupled and obey local symmetry rules. The lowest frequency carbonyl band given by the phosphine substituted complexes are 50–60 cm^{-1} lower in energy than the low energy carbonyl band displayed by the unsubstituted complex. Shifts of this magnitude are generally found upon phosphine substitution and are the result of electronic rearrangements producing more electron density on the transition metal in the case of phosphine substituted complexes. The extremely low frequency of the lowest energy carbonyl band in these complexes suggests that this vibrational mode, as in the tricarbonyl derivative, is associated with a bridging carbonyl group. In benzene solution the infrared spectrum of the L = $PCH_3(C_6H_5)_2$ complex exhibits in addition to bands at 1800 and 1617 cm^{-1} a strong band at 1732 cm^{-1}. The 1732 cm^{-1} band is likely due to the presence of a bis THF adduct since molecular weight studies have shown the tetrakis THF adduct to be highly dissociated in benzene solution. The L = $P(C_4H_9)_3$ derivative displays a much more complex spectrum in benzene than the L = $PCH_3(C_6H_5)_2$ complex. The very strong carbonyl bands at 1791 and 1592 cm^{-1} can be reasonably assigned to a tetrakis adduct containing bridging carbonyl groups. Since this complex undergoes partial dissociation in benzene solution, the additional strong bands at 1737, 1702, 1687, and 1624 cm^{-1} may be associated with lower solvated species, namely, bis and tris THF adducts. The low energy position of the carbonyl bands suggests that carbonyl bridges are retained in the less highly solvated species. In a 10% THF/benzene solvent system the infrared spectrum of $(C_4H_8O)_4Mg(Mo(CO)_2(P(C_4H_9)_3)C_5H_5)_2$ reduces to a two line spectrum with bands at 1791 and 1594 cm^{-1}. The position of these bands suggests that only a tetrakis THF adduct exists in the presence of excess THF. The failure of four-coordinate $Mg{-}Mo(CO)_2(L)C_5H_5$ complexes to adopt a covalent Mg–Mo linkage, as found in the $Mg{-}Fe(CO)_2C_5H_5$ systems, is not well understood but may be the result of the $Mo(CO)_2(L)C_5H_5^-$ group possessing a lower nucleophilicity than the $Fe(CO)_2C_5H_5^-$ group.

$B_4Mg(Co(CO)_3L)$ Complexes. The infrared spectra of the complexes of the general formula $B_4Mg(Co(CO)_3L)_2$ where B = THF, pyridine, and TMEDA and L = an organophosphine or CO are presented in Table III. The infrared spectra of $(C_5H_5N)_4Mg(Co(CO)_4)_2$ in the solid state and in benzene solution are characterized by two strong carbonyl bands near 1930 and 1770 cm^{-1}. These bands are in good agreement with those cited for a toluene solution of $(C_5H_5N)_4Mg(Co(CO)_4)_2$ where two strong bands at 1935 and 1751 cm^{-1} were found.[2] As with $Fe(CO)_2C_5H_5$ and $Mo(CO)_3C_5H_5$ derivatives of magnesium, the simplicity of the infrared spectrum in the carbonyl region suggests that vibrational coupling of the $Co(CO)_4$ groups does not occur. The low energy 1770 cm^{-1} band found in this complex is about 120 cm^{-1} lower in energy than that observed for the $Co(CO)_4^-$ anion.[15] This band is assumed to be associated with the vibration of a bridging carbonyl group ($\mathrm{Mg{-}O{\equiv}C{-}Co}$). Since the tetrakis pyridine adduct is monomeric in benzene solution, a reasonable structure for the complex would be one in which the two $Co(CO)_4$ groups are bonded to axial positions via a bridging carbonyl and the equatorial positions about magnesium are occupied by four pyridine molecules.

The THF, pyridine, and TMEDA adducts of the L = $PCH_3(C_6H_5)_2$ complex are characterized by the presence of three strong carbonyl bands near 1950, 1840–1860, and 1720 cm^{-1} in either the solid state or in solution in THF or benzene. The resolution of three bands is consistent with a ($Mg{-}O{\equiv}C{-}Co(CO)_2L$) arrangement obeying local C_{2v} symmetry. The low energy band near 1720 cm^{-1} is assumed to be associated with the unique bridging carbonyl group while the two higher energy bands are associated with the two terminal carbonyl groups. The simplicity and similarity of infrared spectra given by the THF, pyridine, and TMEDA adducts of the L = $PCH_3(C_6H_5)_2$ complex in benzene and THF suggest that the major solution species are octahedral magnesium complexes possessing bridging carbonyl groups. This contention is supported in the case of the tetrakis C_5H_5N adduct which is found to be only slightly dissociated in benzene solution.

The phosphine substituted complex $(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9)_3))_2$ in the solid state and in THF solution exhibits three strong carbonyl bands near 1930, 1860, and 1710 cm^{-1}. As in the L = $PCH_3(C_6H_5)_2$ complexes, the low energy carbonyl band is assigned to a single bridging carbonyl group (the $Co(CO)_3P(C_4H_9)_3^-$ anion displays a strong broad carbonyl band at 1841 and a shoulder at 1805 cm^{-1} in THF solution). The similarity in the THF solution spectra of the L = $PCH_3(C_6H_5)_2$ and $P(C_4H_9)_3$ complexes with the solid state spectra of the tetrakis THF adducts suggests that the major THF solution species are tetrakis THF adducts. This argument is strengthened by the fact that $(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9)_3))_2$ exhibits monomeric solution behavior in THF.

In benzene solution $(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9)_3))_2$ was found by a combination of conductivity and molecular weight measurements to completely dissociate into a nonionized bis THF adduct. The infrared spectrum of the bis THF adduct in benzene consists of two strong carbonyl bands at 1896 and 1874 cm^{-1} and weak absorptions at 1952 and 1925 cm^{-1}. The absence of a strong carbonyl band near 1710 cm^{-1} is strong evidence that the complex assumes a noncarbonyl bridging structure in benzene solution. The positions of the two strong carbonyl bands are shifted 50–60 cm^{-1} to higher frequencies from those found for the $Co(CO)_3P(C_4H_9)_3^-$ anion. The resolution of two strong carbonyl bands is consistent with the $Co(CO)_3P(C_4H_9)_3$ group obeying local C_{3v} symmetry. These observations lead us to conclude that in benzene the major solution species is a bis THF adduct of $Mg(Co(CO)_3(P(C_4H_9)_3))_2$ containing a direct Mg–Co bond which possesses appreciable covalent character. The ability of the $Co(CO)_3P(C_4H_9)_3$ group and not the $Co(CO)_3PCH_3(C_6H_5)_2$ group to form a direct linkage with magnesium in benzene solution is likely the result of the former group possessing a higher nucleophilicity which favors the formation of four-coordinate magnesium complexes.

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Registry No. $(C_4H_8O)_2Mg(Fe(CO)_2C_5H_5)_2$, 55800-08-3; $(C_5H_5N)_2Mg(Fe(CO)_2C_5H_5)_2$, 37337-07-8; $(C_4H_8O)_4Mg(Mo(CO)_3C_5H_5)_2$, 55800-09-4; $(C_5H_5N)_4Mg(Mo(CO)_3C_5H_5)_2$, 50958-75-3; $(C_4H_8O)_4Mg(Mo(CO)_2(PCH_3(C_6H_5)_2)C_5H_5)_2$, 55800-07-2; $(C_4H_8O)_4Mg(Mo(CO)_2(P(C_4H_9)_3)C_5H_5)_2$, 55800-06-1; $(C_5H_5N)_4Mg(Co(CO)_4)_2$, 55701-38-7; $(C_4H_8O)_4Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$, 55701-39-8; $(C_5H_5N)_4Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$, 55701-40-1; $(C_6H_{16}N_2)_2Mg(Co(CO)_3(PCH_3(C_6H_5)_2))_2$, 55701-41-2; $(C_4H_8O)_4Mg(Co(CO)_3(P(C_4H_9)_3))_2$, 55701-42-3; $(C_4H_8O)_4Mg(Fe(CO)_2C_5H_5)_2$, 55800-05-0; $(C_4H_8O)_2Mg(Mo(CO)_2(PCH_3(C_6H_5)_2)C_5H_5)_2$, 55800-04-9; $(C_4H_8O)_2Mg(Mo(CO)_2(P(C_4H_9)_3)C_5H_5)_2$, 55800-03-8; $(C_4H_8O)_3Mg(Mo(CO)_2(P(C_4H_9)_3)C_5H_5)_2$, 55800-02-7; $(C_4H_8O)_2Mg(Co(CO)_3(P(C_4H_9)_3))_2$, 55701-43-4; $(Fe(CO)_2C_5H_5)_2$, 12154-95-9; $C_5H_5Fe(CO)_2I$, 12078-28-3; C_5H_5N, 110-86-1; $(Mo(CO)_3C_5H_5)_2$, 12091-64-4; $C_5H_5Mo(CO)_2(P(C_4H_9)_3)I$, 31781-53-0; $[Co(CO)_4]_2$, 10210-68-1; $Co_2(CO)_6(PCH_3(C_6H_5)_2)_2$, 31224-11-0; $Co_2(CO)_6(P(C_4H_9)_3)_2$, 14911-28-5; $C_5H_5Mo(CO)_3I$, 12287-61-5; $Mo(CO)_2(C_5H_5)(PCH_3(C_6H_5)_2)I$, 55701-44-5; Mg(Hg), 11146-93-3; Mg, 7439-95-4.

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