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Ligand Effects on CO Bridging in Binuclear Manganese Carbonyl Complexes†

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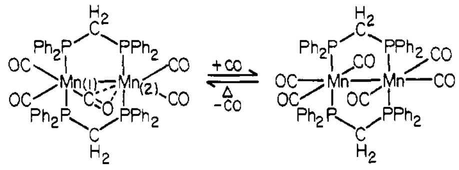
Reactions between $Mn_2(CO)_{10}$, $(C_2H_5)_2PCH_2PPh_2$(depm), and $(c\text{-}C_6H_{11})_2PCH_2PPh_2$(dcpm) (depm = $Et_2PCH_2PPh_2$ and dcpm = $(c\text{-}C_6H_{11})_2PCH_2PPh_2$) in refluxing decane gave binuclear complexes $Mn_2(CO)_6(depm)_2$ and $Mn_2(CO)_5(dcpm)_2$, respectively. A solution of the depm complex could be decarbonylated to give $Mn_2(CO)_5(depm)_2$ whose attempted isolation resulted in disproportionation to the starting hexacarbonyl and unidentified decomposition products. Carbonylation of $Mn_2(CO)_5(dcpm)_2$ afforded $Mn_2(CO)_6(dcpm)_2$ which slowly reverts to the starting pentacarbonyl in the absence of a CO partial pressure. Solutions of both pentacarbonyl complexes show a low frequency (~1640 cm^{-1}) CO stretch assigned to a four-electron bridging carbonyl (4EBC) ligand. Comparing diphosphine ligand electronic and steric characteristics, the steric demand of the ligand appears to dominate as the factor responsible for stabilization of the four-electron bridging carbonyl in dimanganese pentacarbonyl systems.

Introduction

Recent investigations have shown that carbon monoxide can bridge two adjacent metal atoms and act as a four-electron donor ligand. This novel mode of bonding has been referred to as a four-electron μ-bridging carbonyl or 4EBC.[1-3] The first example of this bonding mode was observed in $Mn_2(CO)_5(dppm)_2$ (I), where dppm is $Ph_2PCH_2PPh_2$.[1] This complex contains four terminal carbonyls and the unique CO which binds to one manganese atom through a two-electron σ bond and to the other manganese atom in a "sideways", two-electron π bond. The 4EBC ligand in I is of interest for two reasons. First, the unusual ligand–metal coordination may resemble an intermediate state in the much sought after catalytic hydrogenation of small molecules such as CO or dinitrogen. Second, the 4EBC ligand may also be a model for an important mechanistic intermediate in the ligand substitution reactions of polynuclear organometallic compounds.[4] Both carbon monoxide and isocyanide ligands have been observed to add to I to give $Mn_2(CO)_6(dppm)_2$ (II)[1,3,5] and $Mn_2(CO)_5(RCN)(dppm)_2$ (III),[4] respectively. Both II and III, which contain terminal CO groups, lose CO on heating in hydrocarbon solvent. Complex II reverts to the pentacarbonyl I, while III affords I or $Mn_2(CO)_4(RNC)(dppm)_2$ (IV) depending on the nature of R. Structural investigation of IV has shown that the isocyanide group coordinates as a four-electron-donor bridging ligand.[4]



I II

The $Mn_2(dppm)_2$ core appeared to be an ideal site at which to study the coordination of small molecules. Possibly the Mn–Mn distance is too long to allow formation of conventional, symmetrical CO bridges. Since six CO ligands represent an increase in steric demand about the Mn–Mn core, the steric bulk of the phenyl substituents on the diphosphine ligand could represent the driving force which favors the expulsion of one CO molecule from the equatorial plane of the hexacarbonyl complex.

In order to investigate the effects of ligand electronic and steric properties on CO bonding at this binuclear Mn–Mn site, we reacted $Mn_2(CO)_{10}$ with a series of substituted diphosphine ligands and report our findings here.

Results

Colton and Commons reported the preparations of complexes I and II from the reaction between $Mn_2(CO)_{10}$ and bis(diphenylphosphino)methane, dppm, in refluxing *n*-decane or *p*-xylene.[1]

In a similar manner we prepared dimanganese complexes of $Et_2PCH_2PPh_2$, and $(c\text{-}C_6H_{11})_2PCH_2PPh_2$, depm and dcpm, respectively. Complexes I and II were also prepared for comparison. The new compounds were characterized by their IR spectra (see Table I), by elemental analysis, and where possible by mass spectrometry.

We found that the solubility and apparent stability of the dimanganese complexes were dependent on the particular diphosphine ligands incorporated. The reaction between $Mn_2(CO)_{10}$ and depm in refluxing decane produced, after 6 h, a yellow precipitate characterized as $Mn_2(CO)_6(depm)_2$ (V). Further heating of this mixture for 9.5 h resulted in the formation of a solid which was a mixture of two compounds. These were separated by preparative thin layer chromatography: the higher R_f component was identified as V while the lower R_f component was assigned the composition $Mn_2(CO)_5(depm)_2$ (VI) on the basis of its IR spectrum which showed a carbonyl stretch at 1640 cm^{-1} in CH_2Cl_2. Pentacarbonyl VI was the minor component of the reaction mixture and all attempts to isolate and purify VI resulted in its decomposition to hexacarbonyl V and other unidentified products.

The reaction between dcpm and $Mn_2(CO)_{10}$ in decane at reflux afforded $Mn_2(CO)_5(dcpm)_2$ (VII) as the major product along with small amounts of $Mn_2(CO)_6(dcpm)_2$

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† This contribution is dedicated to the memory of the late Professor Rowland Pettit, whose much valued consultation is deeply missed.

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Table I. Infrared Spectra in the Carbonyl Region

compd	carbonyl stretches, cm^{-1}					solvent[a]
$Mn_2(CO)_5(depm)_2$	1934 m	1897 vs	1856 s	1830 m	1640 m	CH_2Cl_2
	1943 m	1908 vs	1870 s	1844 m	1646 m	mchx
$Mn_2(CO)_5(dcpm)_2$	1933 w	1897 vs	1855 s	1826 m	1646 m (br)	CH_2Cl_2
	1944 m	1906 vs	1869 s	1843 m	1644 m	chx
$Mn_2(CO)_5(dppm)_2$	1940 m	1905 vs	1863 s	1834 m	1649 m	CH_2Cl_2
	1940 m	1902 s	1862 s	1832 m	1648 m	CH_2Cl_2[b]
	1950 m	1919	1879 s	1850 m	1654 m	mchx
$Mn_2(CO)_6(depm)_2$		1917 s	1900 vs	1855 m		CH_2Cl_2
		1925 s	1908 vs	1871 m		mchx
$Mn_2(CO)_6(dcpm)_2$		1912 s	1899 vs	1852 s		CH_2Cl_2
		1918 s	1902 vs	1864 s		mchx
$Mn_2(CO)_6(dppm)_2$	1987 vw	1925 sh	1912 s	1866 m		CH_2Cl_2[b]
$HMn(CO)_3(dcpm)$	1981 vs	1905 s (br)				CH_2Cl_2
	1982 s	1912 s	1906 s			mchx
$HMn(CO)_3(dppm)$	2000 s	1917 s				CH_2Cl_2[b]
	2000 s	1930 s	1920 s			*n*-hexane[b]

[a] chx = cyclohexane, mchx = methylcyclohexane. [b] Reference 1.

(VIII) and $HMn(CO)_3(dcpm)$ (IX). The pentacarbonyl VII was obtained as bright red crystals from the original reaction mixture after concentration and fractional crystallization from CH_2Cl_2–hexane solution. Further concentration of the CH_2Cl_2–hexane filtrate afforded a mixture of red and yellow crystals which were separated mechanically. The yellow crystals were characterized as a CH_2Cl_2 solvate of $HMn(CO)_3(dcpm)$ (IX) by elemental analysis and by comparison of its IR spectrum with that of $HMn(CO)_3(dppm)$.[1] While hexacarbonyl VIII appeared to be the major byproduct from the reaction between $Mn_2(CO)_{10}$ and dcpm (based on thin-layer chromatographic experiments), isolation of VIII from the reaction mixture could not be achieved. An authentic sample of VIII was prepared independently, as will be discussed below.

Pentacarbonyl complex VII, substituted with the dcpm ligand, could be dissolved in benzene, methylcyclohexane, and ether solvents. This finding, together with its relatively straightforward synthesis, made VII a logical choice for carbonylation studies.

Nearly quantitative conversion of VII to VIII was possible in a stirred diglyme or THF solution at room temperature and 1 atm of CO. An analytical sample of VIII was prepared by carbonylation of VII in methylcyclohexane at 165 °C and 3.2 MPa of CO. The recrystallized product, $Mn_2(CO)_6(dcpm)_2$, retained 1 equiv of CH_2Cl_2 and appeared as orange crystals. The decarbonylation of VIII → VII was found to occur over a period of several weeks on exposure of a methylcyclohexane solution of $Mn_2(CO)_6(dcpm)_2$ to air.

Discussion

The net ligand replacement reaction between $Mn_2(CO)_{10}$ and substituted diphosphinomethane compounds is summarized in eq 1. We have not investigated the mechanism

$$Mn_2(CO)_{10} + 2(L\text{–}L) \xrightarrow{-4CO} Mn_2(CO)_6(L\text{–}L)_2 \underset{+CO}{\overset{-CO}{\rightleftharpoons}} Mn_2(CO)_5(L\text{–}L)_2 \quad (1)$$

of this process but we suspect that several discrete intermediates[5] may be involved enroute to the dimanganese hexacarbonyl complex which is substituted with two diphosphine ligands. Once formed, this hexacarbonyl species can decarbonylate to give a dimanganese pentacarbonyl complex with the 4EBC carbonyl ligand.[3] Given suitable conditions an equilibrium (hexacarbonyl ⇌ pentacarbonyl + CO) should be established. We found that under our synthesis conditions, the relative solubilities of the respective dimanganese complexes appeared to be partly responsible for determining which complex was isolated preferentially. Thus in the depm reaction for shorter reaction times, the hexacarbonyl complex precipitated before significant decarbonylation could occur. In the case of the dppm reaction investigated by Colton and Commons[1] the relatively insoluble pentacarbonyl species predominated. Finally, our investigation of the reaction between dcpm and $Mn_2(CO)_{10}$ showed that the pentacarbonyl complex, which was only slightly less soluble than the hexacarbonyl system, precipitated preferentially from decane solution to become the major reaction product.

If fundamental information which can relate ligand structure to the equilibrium between the dimanganese hexacarbonyl and pentacarbonyl complexes is to be gained, then the potential problem introduced by the relative solubilities of these complexes is nontrivial. Nonetheless, based on the results obtained in CH_2Cl_2 solutions (where both complexes appear to have adequate solubility), we believe that the effect of ligand structure on the hexacarbonyl ⇌ pentacarbonyl equilibrium (eq 2) can be assessed.

$$Mn_2(CO)_6(L\text{–}L)_2 \overset{k}{\rightleftharpoons} Mn_2(CO)_5(L\text{–}L)_2 + CO \quad (2)$$

For longer reaction times, the reaction between depm and $Mn_2(CO)_{10}$ afforded a solid which consisted of both $Mn_2(CO)_6(depm)_2$ and $Mn_2(CO)_5(depm)_2$ in roughly equal amounts as determined qualitatively by thin-layer chromatography (TLC). Preparative scale TLC offered a CH_2Cl_2 solution of the pentacarbonyl which showed the 1640-cm^{-1} stretching frequency of the 4EBC carbonyl ligand. Attempts to isolate $Mn_2(CO)_5(depm)_2$ from CH_2Cl_2 resulted in a decomposition reaction(s) which gave the hexacarbonyl complex together with an intractable solid residue. Since the hexacarbonyl species remains soluble in CH_2Cl_2, we conclude that $Mn_2(CO)_6(depm)_2$ is thermodynamically preferred over $Mn_2(CO)_5(depm)_2$.

On the other hand, the equilibrium shown in eq 2 lies more toward the pentacarbonyl species in the cases of dppm and dcpm complexes. Both pentacarbonyl complexes of these ligands are relatively stable in CH_2Cl_2 solution, and both complexes can be carbonylated in a CO atmosphere. For the dppm and dcpm complexes carbonylation can be effected over several hours at room temperature and 1 atm of CO. However, differences were seen in the apparent stabilities of the two hexacarbonyl complexes in CH_2Cl_2. While solutions of $Mn_2(CO)_6(dppm)_2$ appeared relatively stable, the dcpm coordinated analogue, $Mn_2(CO)_6(dcpm)$, slowly decarbonylated over several weeks at room temperature in solution. So comparing the three substituted diphosphine ligands, the equilibrium toward the pentacarbonyl complex is increasingly favored in the order $K^{\mathrm{depm}} \ll K^{\mathrm{dppm}} \lesssim K^{\mathrm{dcpm}}$. This order is consistent with and can be rationalized by the increasing steric bulk of the substituted diphosphine ligands. The larger the substituents on the diphosphine ligand the greater should be the destabilization of the sterically congested hexacarbonyl complex (with six CO ligands in a plane orthogonal to the P–Mn–P bonds) relative to its pentacarbonyl analogue.

It should be noted that the three ligands would also be expected to differ electronically. Tolman's ranking[6] of the relative electron-accepting character of phosphines suggests that for the substituted diphosphinomethane ligands, electron-accepting character should decrease in the order dppm > depm ≳ dcpm. Likewise, the ligands which bear dialkylphosphino groups (dcpm and depm) would be better σ-electron donors than the completely phenyl-substituted ligand, dppm. Considering the metal atoms, more d-electron density should be removed from bimetallic core by two terminally bonded, π-electron-accepting CO ligands than by one four-electron bridging carbonyl group. Therefore, if synergistic donor–acceptor interactions between CO and diphosphine ligands play a significant role in complex stabilization, then the more σ donating, partially alkyl-substituted diphosphine ligands depm and dcpm should stabilize the relatively electron-deficient hexacarbonyl structure, while the more π-accepting ligand, dppm, should stabilize the relatively electron-rich pentacarbonyl complex.

Both the steric and the electronic arguments presented above rationalize the observed preference of the hexacarbonyl in the case of depm and the pentacarbonyl in the case of dppm. That the ligand electronic and steric effects have unequal importance is clearly seen, however, in the case of the dcpm ligand. Electronic effects predict dcpm stabilization of the hexacarbonyl complex while steric effects favor pentacarbonyl stabilization, and the latter is what was observed. In simpler, mononuclear transition-metal complexes, a similar dominance of monodentate phosphine ligand steric effects over electronic effects has been reported.[6]

The Question of Geometric Isomers in $Mn_2(CO)_6(L-L')_2$. Several geometric isomers are possible for dimanganese hexacarbonyl and pentacarbonyl complexes coordinated with two unsymmetrically substituted diphosphinomethane ligands. Assuming that the diphosphine ligands bridge the Mn–Mn site in the hexacarbonyl complexes,[3,5] these ligands may coordinate in either a trans or a cis geometry. The manganese atoms in the trans isomer are equivalent, each being bound to one alkyl-substituted phosphine and one phenyl-substituted phosphine. This isomer, with C_{2h} symmetry, should possess three IR-active carbonyl stretching modes.

In the cis hexacarbonyl isomer the manganese atoms are nonequivalent: one is coordinated by two phenyl-substituted phosphines while the other is coordinated by two alkyl-substituted phosphines. The cis isomer, with C_{2v} symmetry, has six IR-active carbonyl stretching modes, although all six may not be experimentally resolvable. The data summarized in Table I shows that the hexacarbonyl complexes of depm and dcpm both have three resolvable IR stretching frequencies in the carbonyl region. We conclude that the complexes $Mn_2(CO)_6(depm)_2$ and $Mn_2(CO)_6(dcpm)_2$ probably possess trans geometries.

The pentacarbonyl complexes can form one trans and two cis isomers, and in the cis isomers, the 4-EBC ligand can coordinate in two different ways to the nonequivalent manganese atoms (although a $\sigma \rightleftharpoons \pi$ bonding "flip" in the 4EBC could scramble the metal atoms). For each of these three isomers, the lack of symmetry predicts five IR-active carbonyl stretching frequencies. Five distinct CO stretching frequencies were seen, and their sharpness is consistent with the presence of a single isomer. That isomer is probably trans based on its derivation from the presumed trans hexacarbonyl precursor. ^{31}P NMR studies have provided additional insight into the question of diphosphine ligand binding in these binuclear manganese complexes.[3]

Experimental Section

All reactions and manipulations involving phosphines and organolithium reagents were performed under nitrogen by using stainless-steel cannulae and Schlenk techniques. Preparations of manganese compounds were also carried out under nitrogen; however, once formed, these compounds were generally air stable and were handled in air. Dimanganese decacarbonyl (Strem Chemicals) was used without prior purification. The ligands depm and dcpm were prepared from Ph_2PCH_2Li and the appropriate dialkylchlorophosphine employing synthetic conditions analogous to those reported for a similar compound.[7] Intermediate $(c\text{-}C_6H_{11})_2PCl$ was prepared as described in the literature.[8]

Infrared spectra recorded on a Beckman IR 4250 spectrophotometer are given in Table I. NMR spectra were obtained on a Varian A-60 spectrometer. The NMR data is presented in parts per million downfield from internal tetramethylsilane, and apparent resonance multiplicity, relative intensity, and assignment are included in parentheses. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by the Exxon Analytical and Information Division (AID).

Mass spectra were obtained on a Du Pont 21-491 mass spectrometer, using an ionizing energy of 70 eV and an ionizing current of 150 μA. Samples were introduced by a direct insertion probe; perfluorokerosene was employed as a mass marker compound.[9]

$Ph_2PCH_2PEt_2$. A THF–hexane solution containing 44 mmol of Ph_2PCH_2Li[10] was added dropwise under nitrogen to a THF solution containing 5 g (40 mmol) of Et_2PCl. After the solution was stirred at reflux for 2 h, solvent was evaporated, leaving a yellow slurry. Vacuum distillation of this residue through a short-path still afforded 3.2 g (28%) of the diphosphine ligand as a clear, colorless liquid: bp 121 °C (0.01 torr); ^1H NMR ($CDCl_3$) δ 0.8–1.6 (m, 10, CH_2CH_3), 2.13 (s, 2, CH_2), 7.2–7.6 (m, 10, NC_6H_5). Anal. Calcd for $C_{17}H_{22}P_2$: C 70.82; H, 7.69; P, 21.48. Found: C, 70.78; H, 7.73; P, 21.31.

$Ph_2PCH_2P(c\text{-}C_6H_{11})_2$. To a 75-mL solution of 11.7 g (50.3 mmol) of $(c\text{-}C_6H_{11})_2PCl$ in predried THF was added dropwise over a 1-h period 75 mL of a THF–hexane solution containing 55 mmol of Ph_2PCH_2Li. The reaction mixture was heated at reflux for 3 h and then excess lithium reagent was quenched with solid NH_4Cl. Solvent was removed on a rotary evaporator, and vacuum distillation yielded a pale yellow oil: yield 15.0 g (75.2%); bp 210–230 °C (0.07–0.08 torr); ^1H NMR ($CDCl_3$) δ 1.0–2.0 (br m, 22, c-C_6H_{11}), 2.1 (d, 2, CH_2, J_{PCH} = 2 Hz), 7.2–7.7 (m, 10, C_6H_5); mass spectrum, *m/e* 396. Anal. Calcd for $C_{25}H_{34}P_2$: C, 75.73; H, 8.64; P, 15.62; mol wt 396.49. Found: C, 75.98, H, 8.78; P, 14.92.

$Mn_2(CO)_6(depm)_2$. $Mn_2(CO)_{10}$ (0.25 g, 0.64 mmol) and depm (0.5 g, 1.73 mmol) were stirred in refluxing decane (60 mL) for 6 h. The resulting yellow precipitate was filtered, washed with pentane, and vacuum dried; yield 0.38 g (69%). Recrystallization from CH_2Cl_2 and hexane in air resulted in orange yellow crystals: mass spectrum, *m/e* (relative intensity) 770 (62, $Mn_2(CO)_3L_2^+$),

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686 (9, $Mn_2L_2^+$), 398 (23, Mn_2L^+), 343 (34, MnL^+), 55 (100, Mn^+), minor peaks at m/e ca. 826 ($Mn_2(CO)_5L_2^+$), 742 ($Mn_2(CO)_2L_2^+$), 714 ($Mn_2(CO)L_2^+$); peaks due to ligand dissociation were also present. Anal. Calcd for $C_{40}H_{44}O_6P_4Mn_2$: C, 56.22; H, 5.19; Mn, 12.86; P, 14.50. Found: C, 56.51; H, 5.56; Mn, 11.31; P, 13.83.

$Mn_2(CO)_5$(depm)$_2$. $Mn_2(CO)_{10}$ (0.43 g, 1.11 mmol) and depm (0.64 g, 2.22 mmol) were stirred in vigorously refluxing decane (65 mL) for 9.5 h. A mustard colored precipitate formed upon cooling; this solid was filtered, washed three times with pentane, and vacuum dried. TLC on silica gel with 1:1 cyclohexane–toluene as eluent indicated two spots of nearly equal intensity: one orange, R_f = 0.40, and one yellow, R_f = 0.55. The colored bands were extracted from several plates with CH_2Cl_2, and the IR spectra of the resulting solutions indicated the yellow band was $Mn_2(CO)_6$(depm)$_2$ and the orange band, $Mn_2(CO)_5$(depm)$_2$. Attempts to recrystallize the pentacarbonyl resulted in decomposition to the hexacarbonyl and intractable brown material.

$Mn_2(CO)_5$(dcpm)$_2$. $Mn_2(CO)_{10}$ (1.45 g, 3.72 mmol) and dcpm (2.95 g, 7.44 mmol) were combined in 120 mL of degassed decane, and this mixture was heated at reflux with stirring. After 1.25–1.75 h the solvent was removed on a rotary evaporator and the residue was dissolved in a minimum amount of benzene. This solution was passed through a 42.5 mm × 15 mm diameter Florisil chromatography column, eluting with a solution of 5:2 cyclohexane–benzene. Evaporation of the eluate and washing the resulting residue with pentane afforded 2.13 g of orange solid.

TLC on silica gel with 5:2 cyclohexane–benzene indicated at least three components. Compounds were extracted with CH_2Cl_2 from plastic backed plates by cutting up plates into segments each containing only one spot or band. IR spectra of extracted solutions indicated the presence of $Mn_2(CO)_5$(dcpm)$_2$, $Mn_2(CO)_6$(dcpm)$_2$ (the major impurity), and $HMn(CO)_3$(dcpm). Recrystallization of the original impure product from CH_2Cl_2 and hexane by controlled evaporation in air produced bright red crystals of the pentacarbonyl. Further treatment of the recrystallization filtrate is discussed below. Anal. Calcd for $C_{55}H_{88}O_5P_4Mn_2$: C, 63.34; H, 6.57; Mn, 10.54; P, 10.88. Found: C, 63.24; H, 6.65; Mn, 9.81; P, 11.30.

$HMn(CO)_3$(dcpm). The recrystallization solution of $Mn_2(CO)_5$(dcpm)$_2$ was decanted from the red crystals of this compound, and controlled evaporation of the CH_2Cl_2–hexane solvent system produced yellow crystals. Also deposited were a few large red crystals of the pentacarbonyl; these were physically separated from the yellow crystals. The IR spectrum of the yellow crystals in solution indicated no trace of pentacarbonyl VII. Anal. Calcd for $HMn(CO)_3(dcpm)\cdot CH_2Cl_2$ ($C_{29}H_{37}Cl_2O_3P_2Mn$): C, 56.05; H, 6.00. Found: C, 56.22; H, 6.38.

$Mn_2(CO)_6$(dcpm)$_2$. Carbonylation of an unpurified sample of $Mn_2(CO)_5$(dcpm)$_2$ was performed in both cyclohexane solution (0.6 g in 60 mL) and methylcyclohexane solution (1.5 g in 60 mL). In the latter case, the mixture was stirred in a 200-cm^3 Roth bomb under 3.2 MPa of CO and at 165 °C for 4 h. The solvent was removed by rotary evaporation; the residue was washed with hexane to yield an orange solid which had no impurities by IR analysis; yield 0.69 g (46%). Recrystallization in air from CH_2Cl_2 and hexane resulted in orange crystals. Anal. Calcd for $Mn_2(CO)_6(dcpm)_2\cdot CH_2Cl_2$, $C_{57}H_{70}O_6P_4Cl_2Mn_2$: C, 59.23; H, 6.10; Mn, 9.51; P, 10.72. Found: C, 58.83; H, 6.05; Mn, 9.36; P, 10.53.

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Registry No. V, 83291-35-4; VI, 83291-36-5; VII, 83311-75-5; VIII, 83291-37-6; IX, 83291-38-7; $Mn_2(CO)_{10}$, 10170-69-1; Mn, 7439-96-5; depm, 68861-75-6; dcpm, 83291-39-8.

Uncatalyzed and Low-Valent Nickel-Assisted Reactions of α,β-Unsaturated Aldehyde Dimethyl Acetals with Grignard Reagents[†]

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The reactions between the dimethyl acetals of acrolein, crotonaldehyde, dimethylacrolein, 1-cyclohexenecarboxaldehyde, cinnamaldehyde, and benzaldehyde with phenylmagnesium bromide and, on occasion, methylmagnesium bromide under the influence of and in the absence of bis(triphenylphophine)nickel dichloride are described. The methoxy groups are shown to be replaced by phenyl (or methyl) functions at the original carbon–oxygen bond site or a position allylic thereto, and the catalyst is shown not only to enhance the reaction rate of sterically unencumbered acetals but also to affect the regiochemistry.

In continuation of a general study of Grignard reagents with allyl alcohols under the influence of low-valent nickel catalyst,[2,3] the effect of two allylic oxy substituents in the same propene framework on the allylic carbon–oxygen bond-breaking, carbon–carbon bond-forming process became of interest. As a consequence an investigation of the behavior of α,β-unsaturated acetals in the substitution reaction was undertaken.

In view of the known displacement of at least one alkoxy function of such acetals by Grignard reagents alone,[4] the study had to be paralleled by an investigation of the uncatalyzed substitution process. Initially the dimethyl acetals of acrolein (**1a**),[5] crotonaldehyde (**1b**),[6] and di-

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[†] Dedicated to the memory of Professor R. Pettit.

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