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REACTIONS OF BIS(η^4-1,5-CYCLOOCTADIENE)NICKEL(0) WITH TRANSITION METAL HALIDES, AND THE CRYSTAL STRUCTURE OF μ-DICHLORO-BIS(TETRAHYDROFURAN)-HEXACARBONYLDIMANGANESE

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Summary

Bis-(η^4-1,5-cyclooctadiene)nickel(0) reacted with η^5-$C_5H_5Fe(CO)_2Cl$, η^3-$C_5H_5Fe(CO)_3Cl$, $Mn(CO)_5Cl$ and $\{Mn[P(OMe)_3](CO)_4\}_2$ to form metal—metal bonded coupling products. Partial reduction of $Mn(CO)_5Cl$ gave $[MnCl(CO)_3(THF)]_2$ shown to have a chlorine-bridged C_{2h} structure by X-ray diffraction analysis. Ligand transfer also accompanied the reduction of $Fe[P(OMe)_3]_2(CO)_2Br_2$ and $Fe(CO)_4Cl_2$ to $Fe[P(OMe)_3]_2(CO)_3$ and $Fe(CO)_5$, respectively. Only partial reduction was observed for $Ti(acac)_2Cl_2$ and $(\eta^5$-$C_5H_5)_2TiCl_2$ which gave $[Ti(acac)_2Cl]_2$ and $(\eta^5$-$C_5H_5)_2Ti(py)Cl$, respectively.

Introduction

Bis-η^4-1,5-cyclooctadienenickel(0), $Ni(COD)_2$, has been shown to be an effective reagent for coupling aryl [1] and allyl [2] halides. The proposed mechanism for this reaction was the sequential oxidative addition of the organic halide to nickel, followed by reductive elimination of the coupled product. Our continuing interest in the chemistry of metal—metal bonds prompted the examination of the ability of $Ni(COD)_2$ to couple organotransition metal halides forming metal—metal bonds. Metal cluster compounds have been formed under heterogeneous conditions by the action of powdered metals, such as copper, zinc and silver, on metal halides [3]. The alkali metals have been used extensively for the heterogeneous reduction of organometallic halides to form metal—metal bonds [4]. Prior to this work the only other homogeneous reagent that has been shown to couple organotransition metal halides was $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$ [5]. This paper describes the reactions of $Ni(COD)_2$ with various organotransition metal halides and the crystal and molecular structure of one of the reaction products [6].

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Experimental

All manipulations were carried out under a purified argon atmosphere in Schlenk reaction vessels (SRV) [7] that had been flame-dried under vacuum. Solvents were distilled from suitable drying agents [8] directly into the reaction vessels.

All melting and decomposition points were determined under argon in sealed capillaries and are corrected. All IR spectra were obtained using a Perkin-Elmer model 337 spectrophotometer calibrated with polystyrene. Solution spectra were obtained as described previously [8]. Nujol mulls and KBr pellets of solid samples were prepared in a Vacuum/Atmospheres Co. nitrogen-filled dry box. Low resolution mass spectra were obtained with an A.E.I. MS 902 instrument using a solid-probe inlet. Microanalyses were performed by the Materials Science Center Analytical Facility, Cornell University.

Bis-η^4-1,5-cyclooctadienenickel(0) was prepared by the method of Schunn [9]. All other materials were available commercially or were prepared by literature methods.

Reactions of $Ni(COD)_2$ with transition metal halides

General scheme

A sample of metal halide was placed in a dry, argon-filled SRV and degassed in vacuo at least 5 min. A solvent was distilled in and the temperature of the solution/suspension was adjusted. Except as noted, solid $Ni(COD)_2$, weighed by difference in a storage tube, was added all at once to the metal halide solution/suspension. The mixture was stirred magnetically.

The product was isolated either by filtration, using Celite filter aid (Johns-Manville, analytical grade) on a "fine" frit, followed by evaporation of the solvent at reduced pressure with subsequent purification, or by removal of the reaction solvent at reduced pressure followed by similar filtration and purification using another solvent. The reported yield is based on the starting metal halide. Identification of the product was generally done by comparison of the m.p., IR spectrum, and appearance with those of authentic samples or with values in the literature.

η^5-$C_5H_5Fe(CO)_2Cl$. η^5-$C_5H_5Fe(CO)_2Cl$ [10] (0.498 g, 2.35 mmol) was dissolved in THF (10 ml). $Ni(COD)_2$ (0.323 g, 1.14 mmol) was added, and the color immediately darkened and a precipitate formed. The mixture was stirred 4 h at 22°C. An IR spectrum of this solution indicated complete conversion to $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. The solvent was removed at reduced pressure, and the residue was recrystallized from CH_2Cl_2-hexane. This yielded fine, red crystals of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ (0.385 g, 93%), $\nu(CO)$ = 1992s, 1952m, 1785s cm^{-1}.

$[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ (Strem Chemicals, 0.416 g, 1.17 mmol) was dissolved in THF (10 ml). $Ni(COD)_2$ (0.323 g, 1.14 mmol) was added, and the clear, red solution was stirred at 22°C. It quickly became cloudy and opaque, and after 30 min a Ni mirror had formed. An IR spectrum of the solution showed only $\nu(CO)$ for $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$.

η^3-$C_3H_5Fe(CO)_3Br$ [11]. Several experiments were tried, using THF or Et_2O, at temperatures from −78°C to 22°C. The initial scarlet color of $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$ that formed upon mixing gradually gave way to a muddy green, and

no product was isolated from the complex mixture (IR spectrum) that was formed.

η^3-$C_3H_5Fe(CO)_3Cl$. η^3-$C_3H_5Fe(CO)_3Cl$ [12] (0.300 g, 1.39 mmol) was dissolved in Et_2O (30 ml), and the solution was cooled to 0° C. $Ni(COD)_2$ (0.329 g, 1.20 mmol) was added, and the solution quickly turned bright red and a heavy precipitate formed. An IR spectrum of the solution showed some unreacted η^3-$C_3H_5Fe(CO)_3Cl$, so more $Ni(COD)_2$ (~0.1 g, 0.6 mmol) was added in several small portions. A subsequent IR spectrum showed nearly total conversion to $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$. The solvent was removed at reduced pressure, and the residue was dissolved in hexane (40 ml). After filtration, the solution was concentrated to 20 ml at reduced pressure and then cooled slowly to −78° C. Large, garnet-like crystals of $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$ were isolated (0.144 g, 57%), $\nu(CO)$ (hexane) = 2046s, 2011m, 1968vs cm^{-1}, by comparison with literature values [13a] and an authentic sample [13b]. A similar experiment using η^3-$C_3H_5Fe(CO)_3Cl$ (0.343 g, 1.59 mmol) and $Ni(COD)_2$ (0.514 g, 1.87 mmol) yielded 0.200 g of $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$ (70%).

$[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$. $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$ (0.014 g, 0.039 mmol), prepared in the preceding experiment, was dissolved in hexane (5 ml). $Ni(COD)_2$ (0.025 g, 0.091 mmol) was added and the mixture stirred. There was rapid decomposition of the $Ni(COD)_2$ to Ni metal, followed by a gradual deposit of a Ni mirror. An IR spectrum of the solution showed only $\nu(CO)$ for $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$.

$Fe[P(OMe)_3]_2(CO)_2Br_2$. $Fe[P(OMe)_3]_2(CO)_2Br_2$ [14] (0.404 g, 0.780 mmol) in THF (30 ml) was cooled to −15°C. $Ni(COD)_2$ (0.216 g, 0.780 mmol) was added and the mixture was stirred at −15°C. After one hour the solution was a dark, clear, green color with no precipitate. As the solvent was removed at reduced pressure a heavy precipitate formed and a mirror was deposited on the SRV while the solution turned yellow. The solvent was removed at reduced pressure and the residue was recrystallized from hexane (25 ml). A yellow crystalline product was isolated and identified as *trans*-$Fe[P(OMe)_3]_2(CO)_3$, 0.121 g (32%), m.p. 73—74°C (lit. [15] m.p. 71—72°C), $\nu(CO)$ = 1998w, 1919vs, 1910vs (hexane). An IR spectrum of the hexane-insoluble residue showed no $\nu(CO)$.

$Fe[P(OMe)_3]_2(CO)_2Cl_2$. $Fe[P(OMe)_3]_2(CO)_2Cl_2$ [14] (0.330 g, 0.760 mmol) in THF (30 ml) was cooled to 0°C. $Ni(COD)_2$ (0.210 g, 0.760 mmol) was added and the mixture was stirred for 2.5 h at 0°C. After one hour the mixture had turned to a dark, clear, green solution. After further stirring it had become blue and deposited a yellow precipitate. During 2 d of stirring at 0°C the solution became yellow and deposited a mirror on the SRV. The principal product in the solution was *trans*-$Fe[P(OMe)_3]_2(CO)_3$, $\nu(CO)$ = 1913vs, 1907vs (THF). No product was isolated.

$Fe(CO)_4Cl_2$. $Fe(CO)_4Cl_2$ [16] (0.302 g, 1.26 mmol) was suspended in hexane (30 ml) at 0°C. $Ni(COD)_2$ (0.352 g, 1.28 mmol) was added and the mixture was stirred at 0°C for 45 min. A red solution with a dark precipitate quickly formed, and the solution gradually turned light yellow. The solution was filtered and the solvent was removed at reduced pressure, leaving an empty SRV. An IR spectrum of the distillate showed a quantitative transfer of volatile carbonyls identified as $Ni(CO)_4$ [$\nu(CO)$ = 2046vs cm^{-1}] [17] and $Fe(CO)_5$ [$\nu(CO)$ = 2024m, 1999s cm^{-1}].

$Mn[P(OMe)_3]_2(CO)_3Br$. (a) $Mn[P(OMe)_3]_2(CO)_3Br$ [18] (0.600 g, 1.28 mmol) was dissolved in THF (30 ml) and the solution was cooled to 0°C. $Ni(COD)_2$ (0.177 g, 0.64 mmol) was added in 2 portions over 0.5 h. After all the $Ni(COD)_2$ had dissolved an IR spectrum of the clear orange solution showed unreacted $Mn[P(OMe)_3]_2(CO)_3Br$. After stirring 10 h at 22°C there was no visible change, but the IR spectrum indicated some reaction had occurred. The temperature was increased to 45°C over 6 h, and the solution was stirred at that temperature 16 h more. The solvent was removed at reduced pressure and the orange residue was crystallized from hexane (30 ml). A mass spectrum of the orange, crystalline product showed it to be a mixture of $Mn[P(OMe)_3]_2(CO)_3Br$ and $\{Mn[P(OMe)_3](CO)_4\}_2$; the peaks of the latter corresponded closely with those of the reported spectrum [19]. The IR spectrum of the compound also corresponded to the literature values [20]: ν(CO) (hexane) = 1999m, 1971vs, cm^{-1}. The supernatant liquid darkened and decomposed during further workup. (b) $Mn[P(OMe)_3]_2(CO)_3Br$ (0.223 g, 0.48 mmol) was dissolved in THF (20 ml), $P(OMe)_3$ (~0.5 mmol) was added, and the solution was stirred at 50° C. $Ni(COD)_2$ (0.13 g, 0.48 mmol) was added and the mixture was stirred for 34 h. The clear, orange solution became greenish-yellow and deposited a heavy precipitate. The solvent was removed at reduced pressure, and the oily residue was extracted with hexane (25 ml). The filtered solution was cooled slowly to —60° C. An IR spectrum of the orange crystals that formed showed them to be pure $Mn[P(OMe)_3]_2(CO)_3Br$. The solvent was decanted from the crystals and was evaporated at reduced pressure, but attempts to crystallize the oily residue were unsuccessful. A mass spectrum of the oil showed it to be $\{Mn[P(OMe)_3](CO)_4\}_2$ uncontaminated by $Mn[P(OMe)_3]_2(CO)_3Br$.

$Mn[P(OMe)_3]_2(CO)_3Cl$. $Mn[P(OMe)_3]_2(CO)_3Cl$ [21] (0.858 g, 2.03 mmol) was dissolved in THF (30 ml) and the solution was heated to 50°C. $Ni(COD)_2$ (0.505 g, 1.84 mmol) was added and the mixture was stirred for 33 h. The yellow solution rapidly turned orange then red and slowly deposited a heavy precipitate. The solvent was removed at reduced pressure and the residue was crystallized from hexane (30 ml). The orange product was shown to be $\{Mn[P(OMe)_3](CO)_4\}_2$ by its IR spectrum [20], ν(CO) (hexane) = 1998m, 1971vs cm^{-1}. The yield was 0.256 g (43%). The product darkened and decomposed during recrystallization. The supernatant liquid yielded an orange oil with ν(CO) (neat) = 2095m, 2078m, 2070m, 2025s, 1994s, 1962vs(br), ~1901(sh) cm^{-1}. This oil also darkened and decomposed during further workup.

$Mn(CO)_5Cl$. (a) In THF at 22°C. $Mn(CO)_5Cl$ [22] (0.323 g, 1.40 mmol) was dissolved in THF (30 ml). $Ni(COD)_2$ (0.244 g, 0.89 mmol) was added and the mixture was stirred at 22°C. After 10 min all the $Ni(COD)_2$ had dissolved, and an IR spectrum of the clear solution showed that all the $Mn(CO)_5Cl$ had reacted. After 5 min a precipitate began to form. The mixture was stirred a total of 22 h, becoming a clear, light yellow solution with a heavy, dark precipitate. The solvent was removed at reduced pressure and the black residue was extracted with hexane (30 ml). An IR spectrum of the filtered solution showed that the product was pure $Mn_2(CO)_{10}$ [23], ν(CO) = 2044s, 2012vs, 1984s cm^{-1}. Crystallization yielded 0.190 g (69%), m.p. 153—154°C (lit. [24] m.p. 153—154°C). The hexane-insoluble residue was extracted with THF (10 ml), yielding a yel-

low solution having ν(CO) = 2034m, 2020m, 1960m, 1931s cm^{-1}, but no product was isolated. (b) In THF at 0°C. $Mn(CO)_5Cl$ (0.929 g, 4.03 mmol) was dissolved in THF (30 ml) and the solution was cooled to 0°C. $Ni(COD)_2$ (0.563 g, 2.05 mmol) was added and the mixture was stirred one hour at 0°C. The solvent was removed at reduced pressure, and the yellow product was recrystallized from a CH_2Cl_2-hexane mixture to yield 0.761 g (75%) of a compound tentatively identified as $[Mn(CO)_3(THF)Cl]_2$. Anal. Found: Mn, 22.4 (atomic absorption spectroscopy): Cl, 16.2 (neutron activation) Calcd. for $C_{14}H_{16}Cl_2Mn_2O_8$: Mn, 22.28; Cl, 14.38%. Conventional analysis was not possible due to the instability of the compound. The product was further characterized by derivitization as follows: $[Mn(CO)_3(THF)Cl]_2$ (0.216 g, 0.438 mmol) was dissolved in 2,2-dimethoxypropane (DMP, 30 ml). CH_3CN (0.04 ml, 0.05 g, 2 mmol) was added and the mixture was stirred at 22°C. Precipitate formation began within one min. The mixture was stirred 10 h, and the supernatant liquid was removed and discarded. The yellow, powdery product was washed with DMP and dried in vacuo to yield 0.139 g (73%) of a compound with an IR spectrum and m.p. (dec) characteristics identical to an authentic sample of $[Mn(CO)_3(CH_3CN)Cl]_2$ [25].

Ti(acac)₂Cl₂. $Ti(acac)_2Cl_2$ [26] (0.988 g, 3.12 mmol) was dissolved in THF (40 ml) and the solution was cooled to 0°C. $Ni(COD)_2$ (1.797 g, 6.53 mmol) was added, and the clear, orange solution immediately turned dark purple. The mixture was stirred one hour at 0°C, then was allowed to warm to 22°C and stirred 2 h more. The solvent was removed at reduced pressure, and the purple residue was extracted with toluene (180 ml). The toluene solution was concentrated to 30 ml at reduced pressure, heated to reflux to dissolve the crystals that had formed, and allowed to cool slowly to —60°C. The supernatant liquid was decanted, and the product was washed with cold toluene and dried in vacuo to yield 0.630 g (72%) of $[Ti(acac)_2Cl]_2$, m.p. 194—195°C (lit. [27] m.p. 214—215°C). Recrystallization from hot THF raised the m.p. to 210—212°C. The IR spectrum was consistent with that reported in the literature [27]: 1559s(sh), 1514s, 1280s, 1185m, 1021s, 945m, 931s, 868m, 798s, 781s, 740m, 656s, 551m, 452m cm^{-1}.

$(\eta^5$-$C_5H_5)_2TiCl_2$. (a) in THF. Only unreacted starting material was recovered after stirring for 16 h with an excess of $Ni(COD)_2$. (b) In THF under CO. A similar reaction under an atmosphere of CO produced $Ni(CO)_4$ and unreacted $(\eta^5$-$C_5H_5)_2TiCl_2$. (c) In Pyridine. $(\eta^5$-$C_5H_5)_2TiCl_2$ (Research Organic/Inorganic) (0.253 g, 1.02 mmol) was dissolved in pyridine (30 ml) and the clear, orange solution was cooled to 0°C. $Ni(COD)_2$ (0.355 g, 1.29 mmol) was added and the solution was stirred at 0°C for 2 h. The clear, dark red solution was allowed to warm to 22°C, and it quickly became opaque. The mixture was stirred at 22°C for 1.5 h. The solvent was removed at reduced pressure, and the residue was extracted with THF (50 ml). The solvent was removed from the filtered solution at reduced pressure, and the red-brown product was recrystallized from a THF-hexane mixture. The compound rapidly turned yellow upon exposure to air. The m.p. 160—170°C (dec.), air sensitivity, and the presence of pyridine in the product, as indicated by the IR spectrum, suggested that this compound was the same as that reported as $(\eta^5$-$C_5H_5)_2$Ti(py)Cl [28]. No yield was recorded.

Collection of X-ray diffraction data

Clear yellow crystals of $[Mn(CO)_3(THF)Cl]_2$ suitable for X-ray analysis were grown by slowly cooling the reaction mixture. A plate with approximate dimensions 0.2 × 0.2 × 0.05 mm was sealed in a 0.2 mm thinwalled capillary under nitrogen.

Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator (Bragg 2θ angle = 12.2°) using Mo-K_α radiation. Fifteen reflections whose 2θ values ranged from 18.60° to 24.87° were machine-centered and used in least-squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were consistent with those found in preliminary precession and Weissenberg photographs: a monoclinic unit cell with $a = 8.524(1)$ Å, $b = 10.912(2)$ Å, $c = 11.338(1)$ Å, $\beta = 112.80(1)°$, and $V = 972.1(3)$ Å^3. The calculated density of 1.68 g cm^{-3} with $Z = 2$ for $C_{14}H_{16}Cl_2Mn_2O_8$, mw = 493.06, agrees with the experimental density of 1.66 g cm^{-3} measured by the flotation method using a mixture of carbon tetrachloride and iodomethane.

A preliminary rapid scan of reflections out to a maximum 2θ of 25° was examined carefully for systematic absences. The absence of $h0l$ reflections with $l = 2n + 1$ and $0k0$ reflections with $k = 2n + 1$ is consistent only with space group $P2_1/c$ (No. 14) [29]. Since there are only 2 molecules/unit cell, the molecule must be on a crystallographic inversion center, so the asymmetric unit consists of half of a molecule.

Intensity data were collected using ω-scans with X-ray source and monochromator settings identical to those used for the determination of the unit cell parameters. A variable scan rate from 0.99 to 29.30°/min was used, and a scan width of 1.00° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background time equal to scan time. Intensities were calculated from the total scan count (CT) and background counts by the relationship $I = CT - (bgd1 + bgd2)$. The intensities were assigned standard deviations according to the formula $\sigma(I) = [CT + (bgd1 + bgd2)]^{1/2}$. The intensities of three standard reflections (410, $35\bar{1}$, $20\bar{6}$) were monitored every 50 reflections, and data collection was terminated after the observed intensities decayed by 20% from their initial values. The crystal had become quite cloudy. From a total of 1947 reflections collected in one quadrant (h and k positive) of data out to $2\theta = 50°$, 1234 unique reflections were accepted as statistically observed above background on the basis that I was greater than $3\sigma(I)$. Lorentz and polarization corrections were made in the usual manner, but no corrections were made for absorption.

Solution and refinement of the structure

Computations were performed using a combination of standard and local programs [38]; all computations were carried out on a PRIME 400 system. For structure factor calculations, the scattering factors were taken from Cromer and Waber [30]. The agreement factors are defined in the usual way as

$$R = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$$

$R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w(|F_0|)^2]^{1/2}$

In all least-squares refinements the quantity minimized was $w(|F_0| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 4I/\sigma^2(I)$) was employed in calculating R_w and in leastsquares refinement.

Coordinates of the manganese and chlorine atoms were obtained from an E-map following MULTAN. The initial set of starting phases located the Mn and Cl in chemically unreasonable positions. The correct positions were located using the set of starting phases with the next-highest combined FOM. Three cycles of full-matrix least-squares refinement of the coordinates and isotropic temperature factors for these atoms resulted in an R of 0.456 and an R_w of 0.490. The remaining carbon and oxygen atoms were located by means of subsequent difference Fourier calculations and least-squares refinements. A refinement using isotropic temperature factors for all non-hydrogen atoms converged with $R = 0.088$ and $R_w = 0.085$. Anisotropic thermal parameters were introduced, and further refinement followed by a final full-matrix calculation reduced R to 0.042 and R_w to 0.049. No attempt was made to locate the hydrogen atoms. In the final cycle of refinement the maximum parameter shift was 0.12 σ (y coordinate of C(6)). The only features observed in a final difference Fourier map corresponded to THF hydrogen atoms. Final atomic parameters are listed in Table 1; final calculated and observed structure factors are available *. Selected bond distances and bond angles are listed in Tables 2 and 3, respectively. The molecule is illustrated in Figure 1.

Results and discussion

The reaction of $Ni(COD)_2$ with several organotransition metal halides proceeds as anticipated to produce the expected products in good yield. Additionally, the products are easily isolated and purified. η^5-$C_5H_5Fe(CO)_2Cl$ is nearly quantitatively converted to $[\eta^5$-$C_5H_5Fe(CO)_2]_2$. The reductions of $Mn(CO)_5Cl$ to $Mn_2(CO)_{10}$ and η^3-$C_3H_5Fe(CO)_3Cl$ to $[\eta^3$-$C_3H_5Fe(CO)_3]_2$ provide a 70% yield of product.

The synthesis of $[\eta^3$-$C_3H_5Fe(CO)_3]_2$ is more convenient and leads to consistently higher yields than the reported methods [13], even though it was found that the reaction mixture decomposed the $Ni(COD)_2$ quite readily. This problem was overcome by gradually adding a 100% excess of $Ni(COD)_2$. This rapid decomposition may be due to the reaction of $Ni(COD)_2$ or COD with the paramagnetic monomer, η^3-$C_3H_5Fe(CO)_3$, shown [31] to exist in solution in equilibrium with the dimer and known to be reactive towards olefins.

Semmelhack and co-workers [1] had observed that for aryl halides, the iodide was more reactive than the bromide, and the chloride was the least reactive. Also, the solvent that gave the best results for coupling reactions was DMF; no reaction was observed in THF. These results are quite different from what is

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TABLE 1

FRACTIONAL COORDINATES AND TEMPERATURE FACTORS FOR $[Mn(CO)_3(THF)Cl]_2$

Atom	X	Y	Z
Mn	0.5770(1)	0.5977(1)	0.6362(1)
Cl	0.5496(2)	0.6011(1)	0.4175(1)
C(1)	0.7827(9)	0.5307(6)	0.6843(6)
O(1)	0.9159(7)	0.4872(6)	0.7172(6)
C(2)	0.5933(9)	0.5898(6)	0.7981(6)
O(2)	0.6133(8)	0.5831(5)	0.9038(5)
C(3)	0.6733(8)	0.7471(6)	0.6698(6)
O(3)	0.7405(7)	0.8400(5)	0.6949(5)
O(4)	0.3271(5)	0.6659(4)	0.5670(4)
C(4)	0.2023(10)	0.6315(8)	0.6204(9)
C(5)	0.0504(10)	0.7114(9)	0.5533(10)
C(6)	0.1007(10)	0.8064(9)	0.4803(10)
C(7)	0.2874(11)	0.7866(7)	0.5124(10)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	0.0157(2)	0.0066(1)	0.0080(1)	0.0001(1)	0.0046(1)	−0.0007(1)
Cl	0.0224(3)	0.0065(1)	0.0095(2)	−0.0014(2)	0.0079(2)	−0.0006(1)
C(1)	0.0196(14)	0.0085(7)	0.0099(7)	−0.0005(9)	0.0042(8)	−0.0017(6)
O(1)	0.0186(10)	0.0155(7)	0.0198(8)	0.0045(8)	0.0042(8)	−0.0012(6)
C(2)	0.0237(15)	0.0065(6)	0.0101(7)	0.0008(8)	0.0060(8)	−0.0004(6)
O(2)	0.0447(17)	0.0166(6)	0.0089(5)	0.0037(8)	0.0093(7)	0.0007(5)
C(3)	0.0161(12)	0.0089(7)	0.0093(7)	−0.0003(8)	0.0054(8)	−0.0010(6)
O(3)	0.0250(12)	0.0093(5)	0.0147(7)	−0.0051(6)	0.0075(7)	−0.0030(5)
O(4)	0.0152(8)	0.0075(4)	0.0106(5)	0.0007(5)	0.0056(5)	0.0003(4)
C(4)	0.0209(15)	0.0157(11)	0.0205(12)	0.0050(11)	0.0148(12)	0.0054(9)
C(5)	0.0199(16)	0.0153(11)	0.0239(15)	0.0039(12)	0.0111(13)	0.0049(11)
C(6)	0.0189(16)	0.0154(11)	0.0277(14)	0.0057(11)	0.0067(12)	0.0058(11)
C(7)	0.0241(17)	0.0085(8)	0.0274(16)	0.0055(10)	0.0118(14)	0.0063(9)

observed in our system, for which THF is the solvent of choice for most of the reactions; diethyl ether and pyridine were also used successfully. In these studies the bromides tried either produced less product than the corresponding chlorides, or they gave a mixture of unidentifiable materials.

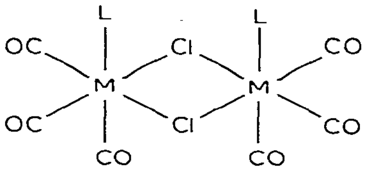
One serious complication in some cases was ligand exchange. This was first encountered when $Fe[P(OMe)_3]_2(CO)_2Br_2$ was reduced to *trans*-$Fe[P(OMe)_3]_2(CO)_3$. It was found to be a severe problem when $Fe(CO)_4Cl_2$ reacted to give $Fe(CO)_5$ and $Ni(CO)_4$. Many of the reactions were found to have produced at least some $Ni(CO)_4$. Attempts to synthesize the unknown tetra-substituted dimer, $\{Mn[P(OMe)_3]_2(CO)_3\}_2$, from $Mn[P(OMe)_3]_2(CO)_3Cl$, failed, producing the known di-substituted complex, $\{Mn[P(OMe)_3](CO)_4\}_2$, instead.

The reduction of $Ti(acac)_2Cl_2$ by $Ni(COD)_2$ produced $[Ti(acac)_2Cl]_2$ with a yield and convenience similar to Salzmann's method [27]. Even with a 100% excess of $Ni(COD)_2$, no further reduction is observed. The reduction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ in pyridine yielded $(\eta^5\text{-}C_5H_5)_2Ti(py)Cl$. This is a significant improvement in convenience over Green's method [28], with a comparable overall yield.

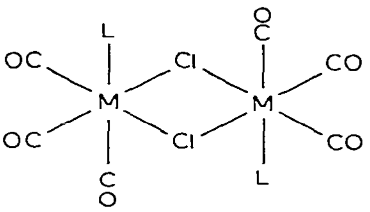
Some systems, notably $\eta^3\text{-}C_3H_5Fe(CO)_3Br$ and $Mn(PMe_2Ph)_2(CO)_3Cl$, produced very complex reaction mixtures from which no product was isolated.

Others, like $Fe[P(OMe)_3]_2(CO)_2Br_2$ and $Mn(CO)_5Cl$, initially gave a solution that had an IR spectrum quite different from the product that was isolated. Attempts to make $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ [28] by the reduction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ in THF were unsuccessful, illuminating a common problem. $(\eta^5\text{-}C_5H_5)_2TiCl_2$, $(\eta^5\text{-}C_5H_5)_2MoCl_2$, and $Ni(PMe_2Ph)_2Cl_2$ all behaved similarly when mixed with $Ni(COD)_2$ in THF: there was an initial, rapid color change, the $Ni(COD)_2$ dissolved, but after stirring a Ni mirror was deposited and only unreacted halide was recovered. Similar behavior was observed for Ph_3SnCl in THF or DMF. This kind of behavior in the reduction of $Mn(CO)_5Cl$ was investigated in detail. By keeping the mixture at 0°C, a novel, unstable compound was isolated. On the basis of Mn and Cl analyses, and the presence of THF, indicated by IR and NMR spectroscopy, the product was tentatively identified as $[Mn(CO)_3(THF)Cl]_2$. This assignment was reinforced by the similarity of the IR spectrum of this compound and that of $[Mn(CO)_3(CH_3CN)Cl]_2$ [25]. Also, when acetonitrile was added to a solution of $[Mn(CO)_3(THF)Cl]_2$ a compound indistinguishable from the known complex, $[Mn(CO)_3(CH_3CN)Cl]_2$ [25], was isolated.

The question of the structure of the compound was not easily resolved by spectroscopy. Two structures are likely for this type of compound, one with C_{2v} symmetry and one with C_{2h} symmetry:



C_{2v}



C_{2h}

Farona and Kraus [25] concluded from the solid-state IR spectrum of $[Mn(CO)_3(CH_3CN)Cl]_2$ that it had C_{2v} symmetry, but Dunn and Edwards [32] proposed C_{2h} symmetry on the basis of its spectrum in solution. Similarly, Hieber and co-workers [33] based their assignment of C_{2h} symmetry to $[Re(CO)_3(THF)Cl]_2$ on the solution spectrum. Because of this uncertainty, a single crystal X-ray structure determination of $[Mn(CO)_3(THF)Cl]_2$ was undertaken.

Structure

The structure determined for $[Mn(CO)_3(THF)Cl]_2$ (Fig. 1) is a modification of that found for $[Mn(CO)_4Br]_2$ [34]. The coordination geometry around each manganese atom is approximately octahedral, and the two octahedra share an edge, bridging through the two chlorine atoms. The THF molecules are located *cis-* to both chlorine atoms and *trans-* to each other. The angles in the manganese-halide cores of the two compounds are virtually identical: the Cl—Mn—Cl′ angle is 84.1(1)° comparable to the average Br—Mn—Br angle of 84.3(3)°, and the Mn—Cl—Mn′ angle of 95.9(1)° is very similar to the average Mn—Br—Mn angle of 95.6(4)°. The average Mn—Br distance, 2.526(10) Å, is longer than the average Mn—Cl distance, 2.397(2) Å, consistent with the greater size of bromine. However, the bridging Mn—Cl bond is signficantly longer than the unbridged Mn—Cl distance of 2.367(4) Å in $Mn(CO)_5Cl$ [35]. Using 2 asymmetric sets, the

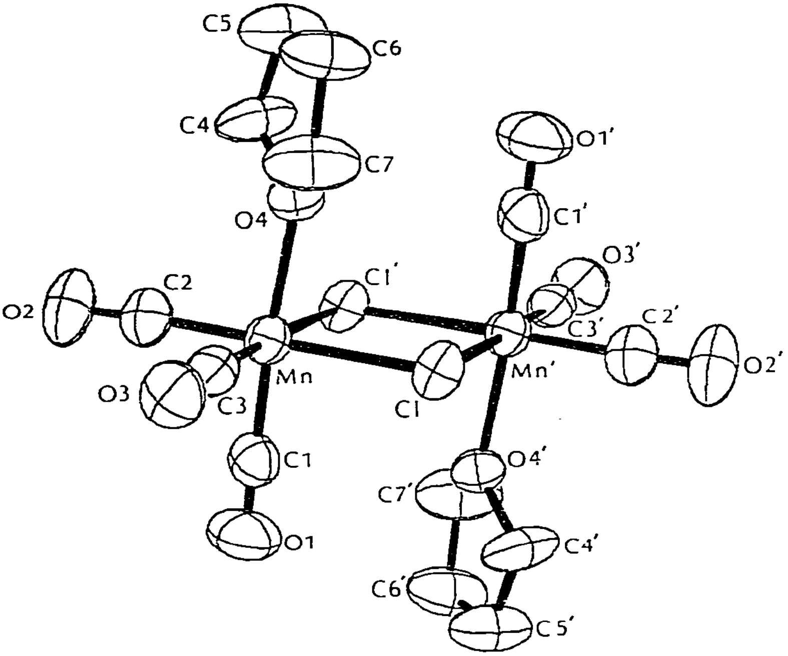


Fig. 1. A perspective view of the $[Mn(CO)_3(THF)Cl]_2$ molecules *.

TABLE 2

BOND DISTANCES IN $[Mn(CO)_3(THF)Cl]_2$

Bond	Length (Å) [a]	Bond	Length (Å)
Mn—Cl	2.399(2)	Mn—Cl'	2.395(2)
Mn—C(1)	1.779(7)	Mn—C(2)	1.789(7)
Mn—C(3)	1.798(7)	Mn—O(4)	2.100(4)
C(1)—O(1)	1.151(9)	C(2)—O(2)	1.149(9)
C(3)—O(3)	1.144(8)	O(4)—C(4)	1.462(12)
O(4)—C(7)	1.438(9)	C(4)—C(5)	1.497(11)
C(5)—C(6)	1.505(16)	C(6)—C(7)	1.504(13)
Mn—Mn'	3.560(2)	Cl—Cl'	3.210(2)

[a] The uncertainty of the least significant figure(s) in given in parentheses.

maximum deviation from the best plane through the twelve atoms in the Mn—Cl—Mn'—Cl' plane is 0.030 Å (C(2)), and the maximum deviation from the best plane through the eight atoms in the Mn—O(4)—Mn'—O(4)' plane is only 0.009 Å (O(1)). The Mn—C and C—O bonds are all within the range of uncertainty of their average bond lengths. The coordination geometry around the manganese is only slightly distorted from octahedral. The THF oxygen (O(4)) is puckered toward the opposite Mn by 0.322 Å from the best plane through its carbon

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* Primed (') atoms are related to unprimed atoms by the inversion operation: ($\bar{x}+1, \bar{y}+1, \bar{z}+1$).

TABLE 3

BOND ANGLES IN $[Mn(CO)_3(THF)Cl]_2$

Atoms	Angle (°) [a]	Atoms	Angle (°)
Cl—Mn—Cl′	84.1(1)	Cl—Mn—C(1)	90.7(2)
Cl—Mn—C(2)	177.8(2)	Cl—Mn—C(3)	93.3(2)
Cl—Mn—O(4)	86.0(1)	Cl′—Mn—C(1)	89.9(2)
Cl′—Mn—C(2)	93.8(2)	Cl′—Mn—C(3)	177.4(3)
Cl′—Mn—O(4)	86.2(1)	C(1)—Mn—C(2)	89.5(3)
C(1)—Mn—C(3)	89.6(3)	C(1)—Mn—O(4)	175.2(2)
C(2)—Mn—C(3)	88.8(3)	C(2)—Mn—O(4)	93.7(3)
C(3)—Mn—O(4)	94.1(2)	Mn—O(4)—C(4)	123.3(4)
Mn—O(4)—C(7)	121.4(5)	C(4)—O(4)—C(7)	109.0(6)
O(4)—C(4)—C(5)	106.0(8)	C(4)—C(5)—C(6)	107.3(8)
C(5)—C(6)—C(7)	105.7(7)	C(6)—C(7)—O(4)	106.7(8)
Mn—C(1)—O(1)	179.0(7)	Mn—C(2)—O(2)	176.9(7)
Mn—C(3)—O(3)	177.2(5)	Mn—Cl—Mn′	95.9(1)

[a] The uncertainty of the least significant figure(s) is given in parentheses.

atoms. This results in Cl—Mn—O(4) angles of only 86° and C(2)—Mn—O(4) and C(3)—Mn—O(4) angles of 94°. The most significant distortion is the small Cl—Mn—Cl′ angle (84.1°). All four C(1)—Mn—(atom) angles are essentially 90°.

The THF molecule is oriented so that it is perpendicular (89.7°) to the Mn—Cl—Mn′—Cl′ plane and nearly perpendicular (87.5°) to the Mn—O(4)—Mn′—O(4)′ plane, being tilted slightly toward Cl′.

The results of this structure analysis lend strong support for the assignment of C_{2h} symmetry to the $[Re(CO)_3(THF)Cl]_2$ [33] and $[Mn(CO)_3(CH_3CN)Cl]_2$ [32] structures.

Conclusion

The reduction of organotransition metal halides with $Ni(COD)_2$ compliments the conventional active-metal reducing agents [3,4] for the formation of metal—metal bonds. It has the advantage over $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_4$ [5] by providing a reaction mixture from which the product may be easily isolated. Some limitations are caused by ligand exchange reactions. The possible extension to other zerovalent nickel complexes, such as $Ni(HPPh_2)_4$ [36] and $Ni(PPh_3)_4$ [37], and the fact that the reactions are solvent and temperature dependent should provide other applications for this technique, depending on proper choice of reagents and reaction conditions.

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