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Hydride Transfer from Transition Metal Hydrides to Dihapto Acyl Ligands

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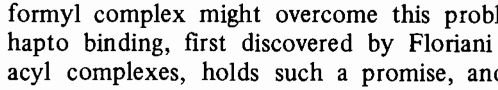
Abstract

The dihapto acyl ligand in $Cp_2Zr[C(O)R]X$, (R = Me, Ph; X = Me, Cl) is subject to hydrogen transfer from Cp_2MH_2 (M = Mo, W), Cp_2ReH and $CpReH_4(PMe_2Ph)$. The initial products are bimetallic dimers of the type $Cp_2XZrOCH(R)ML_n$. The fate of this bimetallic species is highly dependent upon the Group VIB metal when Cp_2MH_2 is the hydride source. For M = Mo, a second hydrogen migrates to the acyl carbon, yielding $Cp_2Zr(OEt)Me$ and products derived from Cp_2Mo. For M = W, C–O bond scission occurs with retention of the W–C bond, to yield the carbene complexes $Cp_2W{=}C(H)R$ along with various oxyzirconium products. Filled d orbitals are not necessary on the hydride source; Cp_2NbH_3 also readily reduces the acyl in $Cp_2Zr[C(O)Me]Me$.

Introduction

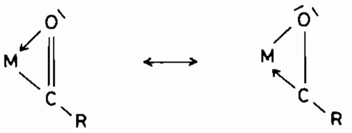
Metal acyl complexes comprise one possible class of intermediates for chain growth in the hydrogenation of carbon monoxide (eqn. 1). Metal formyl complexes (R = H in eqn. 1) are thus to be considered in the initiation of chain growth, but the absence of any



$$\begin{array}{c} O \\ ||| \\ C \\ | \\ M-R \end{array} \longrightarrow M-C(O)R \xrightarrow{H_2} \longrightarrow M-O-CH_2R$$

unequivocal example of this reaction for a transition metal initially served to temper optimism for this mechanism. It has been argued [1] that the strength of the M–H *vs.* C–H bond makes CO insertion into a M–H bond exergonic. On the other hand, any factor which would increase the stability of the formyl complex might overcome this problem. Dihapto binding, first discovered by Floriani [2] for acyl complexes, holds such a promise, and subsequently the first structurally characterized genesis of a formyl ligand from MH and CO involved dihapto (and bridging) binding to an oxophilic early transition metal [3].

While there was an intuitive notion that dihapto acyls ought to be 'activated' towards further hydrogenation relative to classical (monohapto) acyls, very little was actually known about the reactivity of these new acyls. The low infrared stretching frequencies (ν(CO) < 1600 cm^{-1}) [2], as well as the very far downfield (>300 ppm) [4] ^{13}C chemical shifts for these η^2-acyl carbons are consistent with a significant contribution by resonance structure **Ib** to the ground state electron distribution. Also attractive is the fact



Ia **Ib**

that Ti and Zr dihapto acyls form rapidly from CO under mild conditions [2] (25 °C, 1 atm CO), so that the reduction of such an acyl is in essence a reduction of CO itself. We therefore undertook a study of the reaction of such acyls with H_2 and with a variety of transition metal hydrides of Groups VIB and VIIB. Such hydrides offer greater resistance to hydrolysis by H_2O, a likely Fischer–Tropsch product, than the hydrides of zirconium or titanium; they are therefore attractive metals as robust components of a catalytic cycle which produces water or alcohols. We have already reported the results of our attempted reduction of a dihapto acyl by $BH_3 \cdot THF$ [5]. Portions of the present work have been communicated [6, 7].

Experimental

The following complexes were synthesized using literature procedures: $Cp_2Ti[\eta^2\text{-}C(O)Me]Cl$ [2b], Cp_2MoH_2 [8], Cp_2WH_2 [8], Cp_2ReH [8], Cp_2ZrMe_2 [9], $Cp_2Zr(Ph)_2$ [9], $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$ [2], $Cp_2Zr(CO)_2$ [10], $[(CpMoH)_2(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)_2]$ [11], $Cp_2Zr(Me)Cl$ [12], $(Cp_2ZrCl)_2O$ [13], $(Cp_2ZrO)_3$ [14], $Cp_2WH(Ph)$ [15]. All work was performed with rigorous exclusion of air and moisture, unless otherwise noted. $CpReH_4(PMe_2Ph)$, $CpReH_4(PPh_3)$ and $CrReH_2(PMe_2Ph)_2$ were available from other work in this laboratory [16]. Solvents were dried and purified

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as follows: toluene, benzene, tetrahydrofuran and diethyl ether were vacuum distilled from their solutions of sodium benzophenone ketyl. Hexanes (a mixture of isomers) were vacuum distilled from sodium–potassium alloy. Halogenated solvents were dried over P_2O_5 and vacuum distilled, as were the deuterated solvents, C_6D_6, C_7D_8, $CDCl_3$ and CD_3CN. Manipulations were performed in a Vacuum Atmospheres dry box or on a Schlenk line equipped with a source of prepurified nitrogen.

Spectroscopy

Proton NMR spectra were obtained either on a Varian T-60, Varian XL-100, or Varian HR-220 spectrometer. ^{31}P and ^{13}C FT NMR spectra were obtained using the Varian XL-100-A spectrometer. Proton and carbon chemical shifts are reported relative to tetramethylsilane, and ^{31}P chemical shifts are referenced to H_3PO_4 (downfield shifts are given positive values). Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer. Solution spectra were obtained using 0.1 mm path length NaCl cavity cells fitted with airtight septa. Electron impact mass spectra were obtained either from a Varian CH 7 mass spectrometer at Indiana University or from regional facilities at Michigan State University or the University of Nebraska.

Reaction of $Cp_2Ti[C(O)Me]Cl$ (1) with Cp_2MoH_2

A mixture of 50 mg (0.2 mmol) 1 and 45 mg (0.2 mmol) Cp_2MoH_2 in toluene were stirred under N_2 at 25 °C for *ca.* eight hr. The resulting green solution was filtered and the toluene was stripped off, leaving a green residue. This residue was extracted with hexane (3 X 30 mL), from which a green oily solid was obtained upon solvent removal. Infrared and NMR (C_6D_6) analysis showed the presence of Cp_2MoCO [17] (4.18 δ) and Cp_2MoHCl (*vide infra*). In some cases, *small* amounts of $Cp_2Mo(C_2H_4)$ [18, 19] were detected by ^1H NMR (in C_6D_6): 3.93 δ (10H), 1.43 δ (4H).

Cp_2MoHCl

A solution of 100 mg Cp_2MoH_2 in *ca.* 6 mL CH_2Cl_2 was photolyzed for five hr. in a Pyrex Schlenk tube. The CH_2Cl_2 was vacuum removed and a red solid remained. Dissolving the red residue in toluene and eluting this solution through a silica gel column with THF led to the isolation of Cp_2MoHCl as a dark red crystalline solid. NMR (δ, C_6D_6): 4.52 (s, 10H), −8.38 (s, 1H). IR (Nujol): ν(M–H) = 1740 cm^{-1}. Mass spec: m/e = 263 corresponding to $Cp_2{}^{98}Mo^{35}Cl^+$. A green compound remained irreversibly bound to the column. The yields for this reaction varied greatly, with the best yield being 45 mg (39.1%). The analogous reaction in $CHCl_3$ is too rapid to be selective; green Cp_2MoCl_2 is produced.

Reaction of $Cp_2Zr[C(O)Me]Me$ (2) with Cp_2MoH_2

In toluene

A solution of 100 mg (0.4 mmol) Cp_2ZrMe_2 and 90 mg (0.4 mmol) Cp_2MoH_2 in 15 mL of toluene was stirred under 1 atm of CO. Within five minutes, the solution had turned dark green. The toluene was removed under vacuum and the flask was fitted with a sublimer. Sublimation was then attempted at 10^{-4} torr and 25 °C. After *ca.* five hr, the lower regions of the cold finger were coated with a dark green oil. This oil proved to be a mixture of Cp_2MoCO and $Cp_2Zr(OEt)Me$ (4, *vide infra*). All attempts at separating the products of this reaction failed, but all products were readily identified from NMR tube reactions and by comparison of their spectra with those of independently prepared samples.

In CH_3CN

A solution of Cp_2MoH_2 (90 mg, 0.4 mmol) and Cp_2ZrMe_2 (100 mg, 0.4 mmol) in *ca.* 5 mL of CH_3CN was treated with 1 atm of CO. An immediate color change took place. The solution was taken to dryness and the dark oily residue was dissolved in CD_3CN. The entire residue was soluble and $Cp_2Zr(OEt)Me$ (*vide infra*) appeared as the only zirconium-containing product. The molybdenum reaction products consisting of a 2:1 mixture of Cp_2MoCO (4.46 δ, ν(CO) = 1915 cm^{-1}) and $Cp_2Mo(NCCH_3)$ [20] (4.41 δ and 2.68 δ, ν(CN) = 1780 cm^{-1}). An authentic sample of $Cp_2Mo(NCCH_3)$ was made for comparison by photolysis of Cp_2MoCO in CH_3CN.

$Cp_2Zr(CH_3)(OCH_2CH_3)$ (4)

A solution of 25 mg Cp_2ZrMe_2 (0.1 mmol) in C_6D_6 was placed in an NMR tube. To this solution was added 6 μL (0.1 mmol) of dry ethanol (from a fresh bottle of anhydrous ethanol), with immediate gas evolution resulting. NMR analysis showed near-quantitative conversion to 4. NMR (δ, in C_6D_6): 5.75 (s, 10H), 3.83 (q, 2H), 1.00 (t, 3H), 0.32 (s, 3H). In CD_3CN: 6.05 (s, 10H), 3.91 (q, 2H), 1.03 (t, 3H), −0.10 (s, 3H). The identity of the evolved gas was established as CH_4 by the resonance at 0.12 ppm (identical to authentic dissolved CH_4 in C_6D_6).

$Cp_2Zr[C(O)Me]Cl$ (3)

A solution of 250 mg $Cp_2ZrMeCl$ in *ca.* 3 mL of toluene was stirred under 1 atm of CO. A white precipitate formed within 15 min. Stirring was continued overnight and the mixture was filtered under N_2. The solid was washed with hexane, yielding 200 mg (73%) of a dull white powder. NMR (δ, in C_6D_6): 5.48 (s, 10H), 2.25 (s, 3H). IR (Nujol): (ν(CO) = 1556 cm^{-1}).

Formation of $Cp_2(H)WC(H)(Me)OZr(Me)Cp_2$ (9a)

A solution of Cp_2WH_2 in C_6D_6 was treated with solid $Cp_2Zr[C(O)Me]Me$. The resulting spectrum showed the appearance of **9a**. The reaction is complete after *ca.* 30 min. NMR (6, in C_6D_6): 5.83 (s, 10H), 5.40 (q, $^3J_{H-H} = 7$ Hz, 1H), 4.27 (d, $^3J_{H-H} < 1.0$ Hz, 5H), 4.20 (d, $^3J_{H-H} < 1.0$ Hz, 5H), 1.65 (d, $^3J_{H-H} = 7$ Hz, 3H), 0.20 (s, 3H), -10.8 (br, s, 1 H).

$Cp_2W(C_2H_4)$ (11) *from 2 and Cp_2WH_2*

A solution of Cp_2WH_2 (120 mg, 0.4 mmol) and Cp_2ZrMe_2 (100 mg, 0.4 mmol) in 10 mL of toluene was stirred under 1 atm of CO for five hr. The solvent was removed, leaving a dark orange solid. The residue was sublimed to yield 90 mg of an orange crystalline solid. NMR analysis showed this solid to be a 2:1 mixture of $Cp_2W(C_2H_4)$ [19] and Cp_2WH_2 (corrected yield of **11** = **60** mg = 62%). NMR (δ, in C_6D_6): 3.95 (s, 10H), 0.80 (s, 4H, $^2J_{W-H} = 5.1$ Hz).

$Cp_2ReC(H)(Me)OZr(Me)Cp_2$ (8)

A solution of 90 mg 2 (0.3 mmol) and 95 mg Cp_2ReH (0.3 mmol) in *ca.* 3 mL of toluene was allowed to stand for 24 hr. The initially yellow solution turned orange during this time period. Hexane (0.5 mL) was then added dropwise. After 48 hr orange needles had formed. The crystals obtained in this manner were identified by X-ray crystallography [21]. The yield (not optimized) was 60 mg (32%). ^{1}H NMR (6, in C_6D_6): 5.83 (s, 10H), 5.7 (q (7 Hz), 1H), 3.95 (s, 10H), 1.83 (d (7 Hz), 3H), 0.30 (s, 3H). ^{13}C NMR (δ, in C_6D_6) from ^{13}CO enriched synthesis: 59.5 (Re–CH(Me)O–), (d, $^1J_{C-H} = 140$ Hz). E.I. mass spec.: m/e = 344 corresponding to $[Cp_2{}^{187}Re(C_2H_3)]^+$.

$Cp_2(H)WCH(Ph)OZr(Ph)Cp_2$ (9b)

$Cp_2Zr(Ph)_2$ (160 mg, 0.4 mmol) and Cp_2WH_2 (130 mg, 0.4 mmol) were dissolved in *ca.* 5 mL of toluene. The resulting solution was stirred under 1 atm of CO for 20 min. During this time, a color change from yellow to orange occurred. The solution *was* treated with 10 mL hexanes and allowed to stand for one h at which time a yellow solid had formed. Filtration gave 200 mg of 9b (70%). ^{1}H NMR (6, in C_6D_6): 7.1-7.8 (m, 10H), 6.77 (s, 1H), 5.92 (s, 5H), 5.77 (s, 5H), 4.23 (d, $^3J_{H-H} < 1$ Hz, 5H), 4.07 (d, $^3J_{H-H} < 1$ Hz, 5H), – 11.2 (br, 1 H, $^1J_{W-H} = 86$ Hz). A ^{13}C enriched sample (from ^{13}CO) shows that the resonance at 6.77 and -11.2 are coupled to the methine carbon, $^1J_{C-H} = 140$ Hz, $^2J_{C-H} = 5.3$ Hz. ^{13}C NMR: δ 69 ppm (W-CH(Ph)O-), $^1J_{W-C} = 73$ Hz.

Cp_2 W=CHPh (13)

A suspension of 200 mg 9b in 5 mL of toluene was heated to 75 °C for three hr to form a dark green solution and a gray powdery precipitate. The toluene was stripped, leaving a green oil. Extraction of this oil with hexane *(ca. 75* mL) yielded a green solution. About half of the hexane was vacuum removed, at which time a white powder precipitated. Solvent removal was continued until a green solid just started to form. The remaining green solution was filtered and taken to dryness to yield 50 mg of a green solid (45%). This solid is *ca.* 95% pure by NMR. A purer sample may be obtained by recrystallizing from diethyl ether. Crystals suitable for crystallography were obtained from slow evaporation of a C_6D_6 solution. ^{1}H NMR (6, in C_6D_6): 10.82 (s, 1H), 7.02 (br, 5H), 4.65 (s, 5H), 4.58 (s, 5H). ^{13}C NMR (6, in C_6D_6) of the product employing ^{13}CO: 224 (d, $^1J_{C-H} = 131$ Hz, $^1J_{W-C} = 141$ Hz).

$[Cp_2ZrMe]_2O$ (10)

A suspension of 1.0 g $[Cp_2ZrCl]_2O$ (1.9 mmol) in *ca.* 25 mL Et_2O was cooled to 0 °C and 2.9 mL of 1.3 *M* MeLi (3.8 mmol) diluted to 10 mL was slowly added with vigorous stirring. The white suspension turned light yellow and stirring was continued for *ca.* 45 min at 0 “C. The suspension was then filtered through Celite and the precipitate was washed with 5 mL of toluene. The combined Et_2O/toluene filtrate was taken to dryness to yield 400 mg of a light yellow solid (43%). In an alternative synthesis, white crystalline material was obtained by dissolving $Cp_2Zr(CH_3)_2$ in wet CH_3CN. NMR (δ, in C_6D_6): 5.73 (s, 10H), 0.23 (s, 3H). In $CDCl_3$: 5.97 (s, 10H), 0.00 (s, 3H). E.I. mass spec.: m/e = 471 corresponds to $[Cp_2{}^{90}Zr_2MeO]^+$. IR (Nujol): ν(Zr–O) = 740 cm^{-1}.

Hydrolysis of $Cp_2Zr(Ph)_2$

Approximately 20 mg (0.05 mmol) of $Cp_2Zr(Ph)_2$ were dissolved in *ca.* 5 mL of THF and placed in an NMR tube. To this solution was added 1 μL (0.06 mmol) of H_2O. NMR analysis showed the production of C_6H_6, as evidenced by a singlet at 7.23 6. The solution was taken to dryness to yield $[Cp_2ZrPh]_2$-0 [22]. NMR (δ, ppm, C_6D_6): 7.7-7.1 (m, 5H), 5.87 (s, 10H). IR (Nujol): ν(Zr–O) = 723 cm^{-1}.

Reaction of $CpReH_4(PMe_2Ph)$ with 2

A solution of $CpReH_4(PMe_2Ph)$ and Cp_2ZrMe_2 in C_6D_6 was stirred at 25 °C under 1 atm of CO for three days. At this time, the NMR spectrum showed the formation of $Cp_2Zr(OEt)Me$. Also evident were resonances consistent with $CpReH_2(CO)(PMe_2Ph)$: NMR (6 in C_6D_6): 4.58 (s, Cp), 1.68 (d, J = 9 Hz, Me), -10.17 (d, J = 50 Hz, ReH); phenyl protons were obscured by residual benzene. $^{31}P\{^1H\}$ NMR: -20.0 δ (s, splits into a triplet upon hydride coupling).

Cp_2NbH_3 with 2

A solution of $Cp_2Zr[C(O)Me]Me$, 2, in C_6D_6 was treated with equimolar Cp_2NbH_3 to yield an intensely red solution. By NMR, this solution was seen to contain $Cp_2Zr(OEt)Me$. No resonances attributable to Cp-Nb species were observed, and the spectra obtained showed considerable broadening. When the reaction was performed under one atm CO, significant amounts of $Cp_2(CO)NbCH(Me)OZr(Me)Cp_2$ (*vide infra*) were observed.

$Cp_2(CO)NbCH(Me)OZr(Me)Cp_2$

A solution of $Cp_2Nb(H)(CO)$ and Cp_2ZrMe_2 (1: 1) in C_6D_6 was treated with one atm CO. The initially red-brown solution immediately turned green. ^1H NMR examination indicated quantitative formation of $Cp_2(CO)NbCH(Me)OZr(Me)Cp_2$. NMR (δ, in C_6D_6): 5.83 (s, 5H), 5.79 (s, 5H), 5.12 (q, 1H, J = 6.5 Hz), 4.68 (s, 5H), 4.63 (s, 5H), 1.62 (d, 2H, J = 6.5 Hz), 0.10 (s, 3H). IR: (C_6D_6): $\nu(CO) = 1894$ cm^{-1}.

X-ray Structure Determination of Cp_2 WC(H)Ph

Crystal data and parameters of the data collection (at – 160 °C, $5 \leqslant 2\theta \leqslant 50°$) are shown in Table I. Crystal handling prior to and during data collection was carried out in a nitrogen atmosphere; data collection and processing techniques have been described [23]. The largest variation among four standard reflections was 0.4 σ. Two complete data sets were collected, the first (from the larger crystal) being used to solve the structure by direct and Fourier methods. Attempts at introducing anisotorpic thermal parameters for carbon atoms yielded non-positive definite parameters for several carbons, even with correction for absorption. The second complete data set (using a smaller, nearly equidimensional crystal) also yielded unacceptable anisotropic temperature factors for several carbons. The final model chosen (results reported here, using second crystal) employed anisotropic refinement of tungsten only. Hydrogen atoms were neither located nor included in calculated positions. The final difference Fourier was essentially featureless, the major peaks being in the vicinity of the tungsten atom. Difference Fourier sections through the planes of the Cp rings gave no evidence for any resolvable disorder.

TABLE I. Crystal Data for $(C_5H_5)_2WC(H)(C_6H_5)$.

Formula	$C_{17}H_{16}W$
Color	Emerald green
Crystal dimensions (mm)	0.08 X 0.08 x 0.08
Space group	P_{cab}
Cell dimensions (at -160. C; 5lreflect.)	
a	13.967(4) A
b	11.286(3)
c	16.327(4)
Molecules/cell	8
Volume	2573.7
Calculated density (gm/cm^3)	2.086
Wavelength	0.71069 A
Molecular weight	404.16
Linear absorption coefficient	91.5
Number of reflections collected	3561
Number of unique intensities	1686
Number with F > 0.0	1420
Number with F > sigma (F)	1247
Number with F > 2.33 sigma (F)	1075
Final residuals	
R(F)	0.0529
*R*w(F)	0.0483
Goddness of fit for the last cycle	1.026
Maximum Δ/σ for last cycle	0.05

The results of the X-ray study are shown in Tables II and III and in Figs. 2 and 3. Cp ring carbons are coplanar to within 1 cr. Phenyl carbons are coplanar to within 1.7 σ, and the carbene carbon (C2) lies within 1 σ of the phenyl plane. The Cp two ring centroids, W and C2 deviate from their mutual least squares plane by less than 1 σ. Metal to ring-midpoint lines intersect the ring planes at angles of 88.2” and 88.7”. The phenyl ring plane makes an angle of 77.9” with the plane of Cp(1), Cp(2), W and C2. For full detail of the structural study, write Chemistry Library, Indiana University, requesting Molecular Structure Center report number 81017.

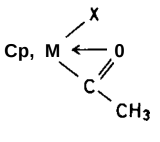
TABLE II. Fractional Coordinates and Isotropic Thermal Parameters for $Cp_2WC(H)Ph$.

	$10^4 x$	$10^4 y$	$10^4 z$	IO B_{iso}
W	2236(1)	1177(1)	2581.9(5)	10
C(2)	2469(18)	1410(20)	1353(13)	19(5)
C(3)	3229(20)	1956(23)	892(14)	18(5)
C(4)	4083(20)	1259(27)	697(15)	29(5)
C(5)	4830(22)	1828(26)	244(16)	26(6)
C(6)	4734(19)	2974(25)	–53(15)	24(6)
C(7)	3888(20)	3610(23)	96(14)	24(5)
C(8)	3107(19)	3053(23)	548(14)	20(5)
C(9)	3878(17)	1417(20)	2662(14)	17(5)
C(10)	3587(17)	723(21)	3368(13)	12(4)
C(11)	2980(17)	1489(20)	3814(12)	13(4)
C(12)	2843(19)	2621(22)	3407(13)	20(5)
C(13)	3436(17)	2592(21)	2700(14)	19(4)
C(14)	1049(17)	–50(21)	2084(13)	14(5)
C(15)	1327(16)	–433(19)	2877(12)	9(4)
C(16)	1078(19)	447(23)	3418(15)	17(5)
C(17)	629(20)	1434(23)	3039(15)	23(5)
C(18)	666(18)	1100(23)	2147(13)	18(4)

Results and Discussion

While the acyl complexes employed here do not react with molecular hydrogen at 25 °C and 1 atm, heterobimetallic hydrogen transfer from a variety of Group V-VIIB hydride occurs readily. As described earlier [6] several iron or cobalt η^1-acetyl complexes are not reduced by these same hydride complexes, so the Lewis acid function of early transition metals in η^2-acyl ligation performs an essential role.

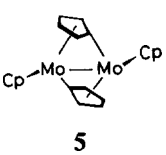
The first dihapto acyl investigated was Cp_2Ti-[C(O)Me]Cl **(1).** This complex was found to be unreactive toward H_2 at room temperature in THF



1 M = Ti, X = Cl
2 M = Zr, X = CH_3
3 M = Zr, X = Cl

and at 80 °C in toluene. Stirring for long periods of time under H_2 in both cases led only to decarbonylation to $Cp_2Ti(Me)Cl$. Attempts to reduce **1** using $NaBH_4$ or $BH_3 \cdot THF$ yielded uncharacterized species whose color and lack of NMR signal indicated reduction to Ti(III) had taken place. Attempts to effect hydride transfer utilizing Cp_2MoH_2 again led to disappearance of NMR-observable titanium species along with the formation of a mixture of molybdenum complexes, among which were identified Cp_2MoCO and Cp_2MoHCl. In some experiments, a small amount of $Cp_2Mo(C_2H_4)$ [17–19] was detected.

The above evidence for undesirable reduction of Ti(IV) and for halide transfer in the attempted hydrogenation of the acyl in **1** led us to examine the zirconium acyl complex 2. Not only in this complex free of chloride ligand, but Zr(IV) is more resistant to reduction than is Ti(IV) [24]. Indeed Cp_2Zr[C-(O)Me]Me (2) was found to react smoothly with Cp_2MoH_2 at 25 °C to form $Cp_2Zr(OCH_2CH_3)CH_3$ (4). Neither methane nor acetaldehyde are detectable products. There appeared to be two major molybdenumcontaining products formed. The predominant one was immediately identified as Cp_2MoCO. The ^1H NMR spectrum of the other Mo complex showed resonances indicative of both π bound (pentahapto) and σ bound (monohapto) cyclopentadienyl ligands. Comparison of this spectrum with that obtained from an independently synthesized sample showed this complex to be $\{[(\eta^5\text{-}C_5H_5)Mo]_2[\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)]_2\}$ (5) [11]. It was found that hydrides 6 [11] and 7 [11], each of which is a source of 5 under other reaction conditions (*vide infra*), were unreactive toward 2 under conditions where 2 reacts with Cp_2MoH_2; 6 and 7 thus cannot be intermediates in the reaction.



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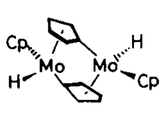

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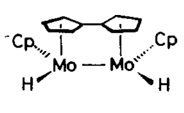
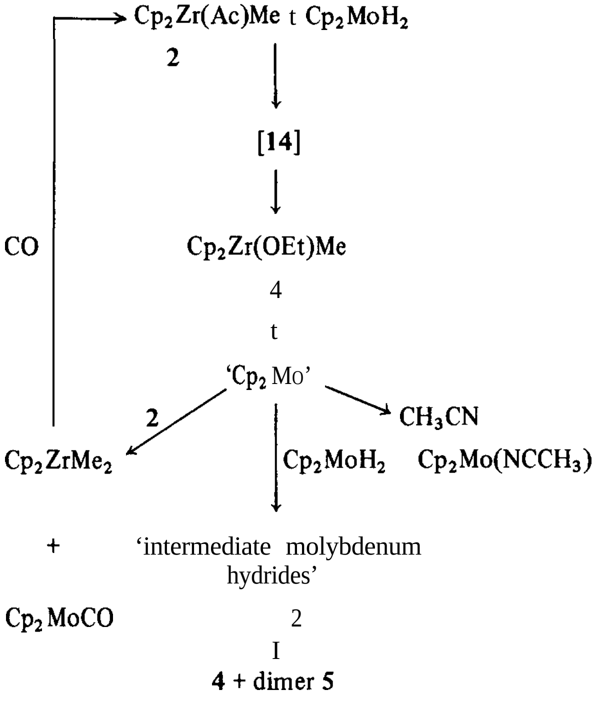


7

When the reaction was performed under N_2, a substantial amount of Cp_2ZrMe_2 was produced, in addition to the products noted above. Conversely, performing the reaction under one atm of CO led to complete conversion (NMR evidence) of acyl 2 to $Cp_2Zr(OEt)Me$, 4. Similar results were obtained when solutions of Cp_2ZrMe_2 and Cp_2MoH_2 were treated with CO [25].

The production of $Cp_2Zr(OEt)Me$ from the equimolar reaction of $Cp_2Zr[C(O)Me]Me$ and Cp_2-MoH_2 suggests the possible intermediacy of Cp_2Mo, 'molybdenocene'. The chemistry of molybdenocene generated by other means is now well documented and the variety of molybdenum products observed here are consistent with its known high reactivity [11]. For example, we find that in hydrocarbon solvents, the molybdenocene fragment is scavenged either by acyl complex 2 or by Cp_2MoH_2. These results are detailed in Scheme I. With 2, decarbonylation to Cp_2ZrMe_2 occurs with simultaneous formation of Cp_2MoCO. With Cp_2MoH_2, dimerization



Scheme 1

occurs to ultimately produce complex 5. It should be noted that the formation of complex **5** indicates delivery of three moles of H_2 to the acyl ligands for every two moles of Cp_2MoH_2 consumed. This stoichiometry is in line with our observation that more than one mol of ethoxide is formed for every mol of Cp_2MoH_2 that is consumed [6]. The extra reducing power derives from active involvement of the Cp rings and ultimate transfer of hydrogen from these rings to the acyl moiety. Compound 14 is included in Scheme I as a proposed bimetallic intermediate corresponding to transfer of one hydride from molybdenum to the acyl carbon (see later).

The foregoing describes the fate of molybdenocene in hydrocarbon solvents. We find that the fragment 'Cp_2Mo' exhibits different selectivity in coordinating solvents. For example, a stirred solution of Cp_2ZrMe_2 and Cp_2MoH_2 (each 0.08 *M*) under one atm of CO yields Cp_2MoCO as the predominant Mo product ***even in neat*** CH_3CN. Only 25% of the molybdenum is found as $Cp_2Mo(NCCH_3)$ under these conditions. A dramatic change occurs upon performing the same reaction under only 0.1 atm CO since carbonylation of Cp_2ZrMe_2 is now slower than the reaction of the acetyl complex with Cp_2MoH_2. In this case, the mol ratio Cp_2MoCO:$Cp_2Mo(NCCH_3)$ is 1:2. The yield of ethoxide 4 in both cases is nearly quantitative. Thus, by maintaining a low concentration of the acyl complex, the scavenging of molybdenocene by solvent is favored. Interestingly, Cp_2MoH_2 is unable to compete with solvent for Cp_2Mo, since no observable amounts of the dimeric Mo complex **5** are seen in acetonitrile solvent.

The reaction proceeded similarly when $Cp_2Zr[C(O)CH_3]Cl$ (3) reacted with Cp_2MoH_2. There was no evidence of chloride transfer to molybdenum as was seen using $Cp_2Ti[C(O)Me]Cl$. A characteristic of this reaction was that more of the dehydrogenated dimer 5 was formed; correspondingly less Cp_2MoCO was formed. A corollary observation is that not only $Cp_2Zr(OCD_2CH_3)Cl$, but also $Cp_2Zr(OCHDCH_3)Cl$ was produced when Cp_2MoD_2 [26] was used as the reducing agent. $Cp_2Zr(OCHDCH_3)Cl$ was evident as a doublet ^1H NMR (220 MHz) methyl resonance flanking the central pseudosinglet of $Cp_2Zr(OCD_2CH_3)Cl$. The P-hydrogen in $Cp_2Zr(OCHDCH_3)Cl$ originates from the Cp ring on molybdenum, and accounts for the observed enhancement of ethoxide produced relative to Cp_2MoH_2 employed when $Cp_2Zr[C(O)CH_3]Cl$ is the substrate.

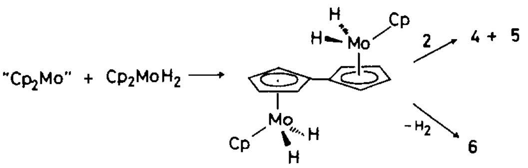
It is not immediately apparent why complex 3 leads to more Mo_2 dimer (5) than does 2. The smaller yield of Cp_2MoCO when using the chloride acyl 3 is not consistent with the independent observation [27] that 3 is more easily decarbonylated than 2 (eqn. 2, $K_{Cl} > K_{Me}$). These results rule out the possibility that Cp_2MoCO is formed from scavenging

$$Cp_2Zr(Ac)X \overset{K}{\rightleftharpoons} Cp_2ZrMeX + CO \qquad (2)$$

$$X = Me, 2 \qquad x = Cl, 3$$

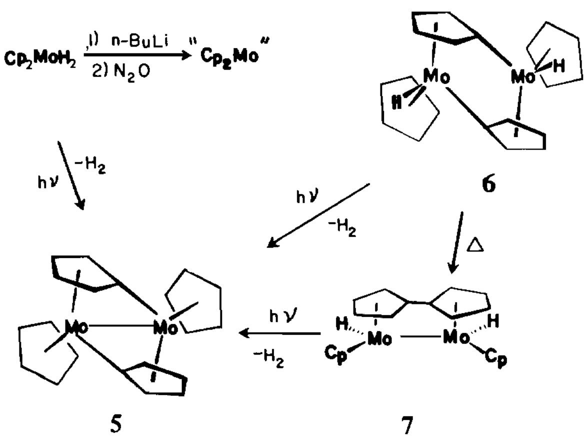
free CO formed in eqn. 2. In fact, these results suggest that Cp_2MoCO is formed by direct decarbonylation of the acyl species, and this has therefore been incorporated into Scheme I.

The lack of reactivity of the dimeric molybdenum hydrides 6 and 7 with 2 is of significance with regard to the 'intermediate molybdenum hydrides' noted in Scheme I. Scheme II shows some chemistry of molybdenocene as determined by Berry *et al.* [11]. Since neither 6 nor 7 react with 2, some previously unobserved reactive intermediate must form in the presence of Cp_2MoH_2 ***before*** complex 6 is formed. One such pathway is proposed in eqn. 3. The demonstrated ability of Cp rings to couple, but subsequently cleave (7 → 5 in Scheme II) is reassuring in light of the complicated chemistry required for eqn. 3.



(3)

By employing Cp_2ReH, it is possible to establish the stepwise character of the acetyl → ethoxide conversion and to produce a bimetallic complex of sufficient stability to allow isolation and structural characterization [21] (Fig. 1 and eqn. 4). The IR spectrum



Scheme 2

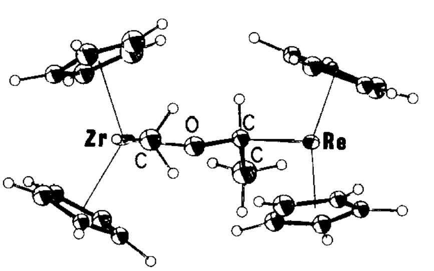
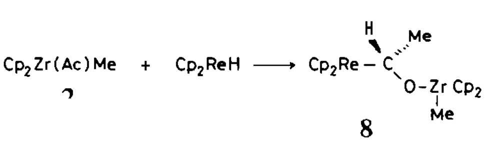
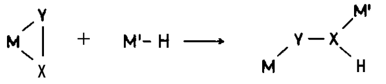


Fig. 1. Molecular structure of $Cp_2MeZr(OCHMe)ReCp_2$.



$$Cp_2Zr(Ac)Me + Cp_2ReH \longrightarrow Cp_2Re{-}C(H)(Me){-}O{-}Zr(Me)Cp_2 \qquad (4)$$

of this complex exhibits a very strong band at 1030 cm^{-1}, consistent with a single bond carbon-oxygen stretch. At 60 MHz, this complex shows only a single resonance for protons on the inequivalent (diastereotopic) Cp rings on zirconium [28]; however, at 220 MHz, the resonance at 5.83 δ can be resolved into two peaks separated by 0.0016 ppm. Both rhenium and hydrogen are added to the acetyl carbon to form 8 (eqn. 4). Geminal addition of the M'-H bond to a coordinated ligand (eqn. 5) is a reaction which has not been carefully documented to date. In fact, eqns.

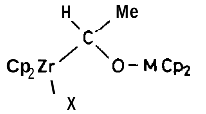


(5)

4 and 7 (see below) may not represent elementary steps and the geminal addition product may not be the primary one. The work of Floriani [29] and of Schwartz [30] shows that a bridging ‘aldehyde’ moiety undergoes rapid degenerate rearrangement

(6)

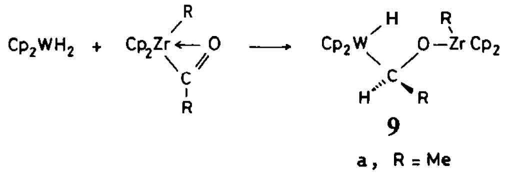
(eqn. 6) when M = M' = Cp_2ZrCl. It is therefore possible that, if acyl hydrogenation initially produces **II** by vicinal additon across the C⋯O bond, such a kinetic product could rapidly rearrange to the observed (thermodynamic) product.



M = Re, WH, MoH

II

An attempt was next made to capitalize on the enhanced stability of third row transition metal complexes (relative to second row analogs) in order to detect an analog of 8 for a dihydride complex. With Cp_2WH_2, the bimetallic hydride 9a is indeed detectable (eqn. 7). This complex is the direct analogue of the postulated intermediate 14 (Scheme I), and a rather rare example of a *cis*-hydridoalkyl complex. This reaction was characterized by a color change

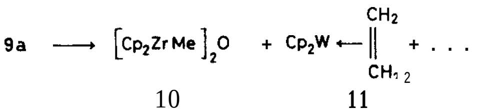


(7)

9

a, R = Me
b, R = Ph

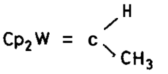
from yellow to orange. Complex 9a showed considerable instability and was never isolated. Its decomposition followed promptly after its formation, to yield $[Cp_2Zr(CH_3)]_2O$ (**10**) and $Cp_2W(\eta^2\text{-}C_2H_4)$ (**11**). The use of ^{13}CO led to carbon-13 incorporation in the ethylene ligand of **11** to produce the non-first-order ^1H NMR [31] of coordinated $H_2{}^{13}C^{12}CH_2$. Additional resonances were observed in the zirconium cyclopentadienyl region as reaction 8 proceeded and the ^1H NMR resonances of methane and cyclopentadiene also appeared. The resonance of $(Cp_2ZrO)_3$ [14] was not present. Similar resonances were observed when either Cp_2ZrMe_2 or $(Cp_2ZrMe)_2O$ was hydrolyzed. By proton NMR, the formation of **11** was nearly quantitative, while 10 accounted for approximately two-thirds of the original zirconium cyclopentadienyl peak intensity.



(8)

10 11

Periodic spectroscopic monitoring of the course of eqn. 8 allowed detection of an intermediate (12) whose two C_5H_5 resonances appear in the region characteristic of biscyclopentadienyl tungsten complexes. These closely spaced resonances at 4.59 δ and 4.63 δ were accompanied by a doublet at 1.03 δ (J = 6 Hz), and a quartet at 10.3 δ (J = 7 Hz) with the relative intensities being 5 :5:3: 1. The far downfield quartet at 10.3 δ is in the region usually associated with α-hydrogens on metal carbenes [32] and we assign the structure shown to 12. Complex 12 rearranges quickly (minutes) to the ethylene complex 11

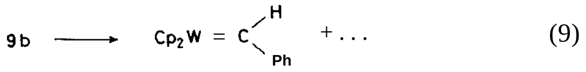


12

[33]. The mechanism of formation of the oxo-bridged zirconium dimer 10 in eqn. 4 is not clear. A heterolytic mechanism, passing through the ion pair $\{Cp_2WH(CHMe)^+, Cp_2Zr(Me)O^-\}$, has been briefly discussed [7]. However, in the light of recent work by Erker [34], homolysis to the radicals $Cp_2W(H)(CHMe)$ and $Cp_2Zr(Me)O$ cannot be excluded. Our attempts to scavenge any *free* radicals in reaction 8 with 1,4-cyclohexadiene were unsuccessful.

The 1,2 hydrogen shift in the isomerization 12 → 11 is unusual, but not unprecedented [35]. It is possible to prevent this rearrangement, and thus isolate a Cp_2W(carbene) complex analogous to 12. Reaction of $Cp_2Zr[C(O)Ph]Ph$ (prepared *in situ* from $Cp_2Zr(Ph)_2$ and CO) with Cp_2WH_2 yields the expected bimetallic complex 9b. Thermolysis of 9b in C_6D_6 at 70 °C for three hr. (or 100 °C for 15 min) leads to the formation of a green solution from which carbene complex 13 can be isolated (eqn. 9). Proton and ^{13}C

NMR of 13 were consistent with the formula shown. As with **9a**, the reaction yields a complex mixture of zirconium products (none of which is $[Cp_2ZrPh]_2O$), but it is clean with respect to tungsten, and crystals of 13 suitable for X-ray diffraction can be obtained.



$$9b \longrightarrow Cp_2W=C(H)Ph + \ldots \quad (9)$$

Figure 2 shows an ORTEP drawing of 13. The orientation of the carbene ligand is such that the cyclopentadienyl rings are inequivalent, consistent with the NMR spectra of both 12 and **13.** This orientation of the carbene plane (within 6.3” of coplanarity with W and the two ring midpoints) is in accord with published molecular orbital calculations [36] and is identical to that found [37a] in $Cp_2W{=}C(H){-}OZr(H)(C_5Me_5)_2$, 16. Table III shows some pertinent bond lengths and angles. The W-C bond distance for the carbene is 2.05(2) A, comparable to 2.00(1) in 16 and significantly shorter than the W-C distance of 2.15(2) reported for $(CO)_5W{=}C(Ph)_2$ [37b]. The Cp-W-Cp angle of 143.3’ is again large, as it is for the Cp_2Re fragment in 8. It should be noted that both complexes are formally d^4, but the electronic requirements of the carbene ligand may account for the slightly smaller angle in **13,** which indicates decreased electron density about the metal. Drawings of space-filling models (Fig. 3) reveal the

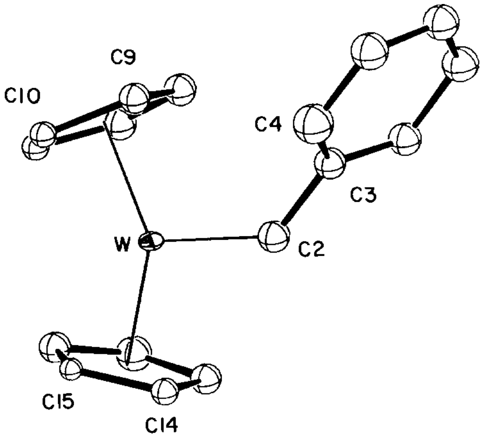


Fig. 2. ORTEP drawing of $(\eta^5\text{-}C_5H_5)_2WC(H)C_6H_5$. The hydrogen atoms, including the single hydrogen known to be on C(2) from NMR data, are not shown. Unlabeled carbons follow the sequence indicated by those which are labeled.

TABLE III. Bond Distances (A) and Selected Bond Angles (deg) in $Cp_2W{=}CH(Ph)$.

W	C(2)	2.05(2)			
W	C(9)	2.31(2)	C(9)	C(10)	1.45(3)
W	C(10)	2.34(2)	C(9)	C(13)	1.46(3)
W	C(11)	2.29(2)	C(10)	C(11)	1.41(3)
W	C(12)	2.28(2)	C(11)	C(12)	1.45(3)
W	C(13)	2.32(2)	C(12)	C(13)	1.42(3)
		avg. 2.31			avg. 1.44
W	C(14)	2.31(2)	C(14)	C(15)	1.42(3)
W	C(15)	2.27(2)	C(14)	C(18)	1.41(3)
W	C(16)	2.27(2)	C(15)	C(16)	1.37(3)
W	C(17)	2.38(3)	C(17)	C(16)	1.42(4)
W	C(18)	2.31(3)	C(17)	C(18)	1.50(3)
		avg. 2.35			avg. 1.42
C(2)	C(3)	1.44(4)			
C(3)	C(4)	1.46(4)			
C(3)	C(8)	1.37(4)			
C(4)	C(5)	1.43(4)			
C(5)	C(6)	1.39(4)			
C(6)	C(7)	1.40(4)			
C(7)	C(8)	1.46(4)			
		avg. 1.42			
Cp(1)[a]	W	Cp(2)	143.3”		
Cp(1)	W	C(2)	109.1		
Cp(2)	W	C(2)	107.6		
W	C(2)	C(3)	133(2)		

[a] Defined as the center of the Cp ring made up of C(9)-C(13).

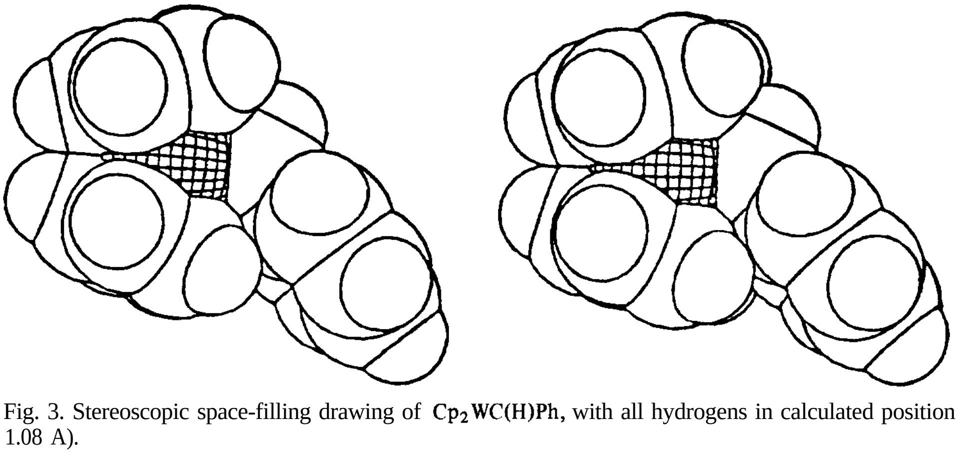


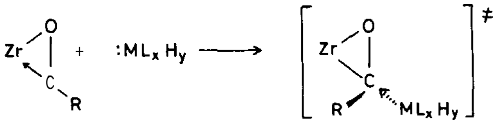
Fig. 3. Stereoscopic space-filling drawing of $Cp_2WC(H)Ph$, with all hydrogens in calculated positions (taking a C-H distance of 1.08 A).

steric origin of the phenyl ring conformation to be Cp/Ph contacts.

The difference in reactivity between Cp_2WH_2 and Cp_2MoH_2 (more specifically, between bimetallic complexes 9 and 14) is striking. Complex 14 reacts further by rapid reductive elimination of the ethoxide 4 (Scheme I), while complexes 9a and 9b react *via* cleavage of the carbon-oxygen bond (eqn. 8). This difference can be attributed to the relative stabilities of molybdenocene and tungstenocene. Tungstenocene is much more reactive (thus of presumably higher energy) than is molybdenocene. In fact, recall that Cp_2Mo generated here scavenges CO in both benzene and acetonitrile, *i.* e. : it survives long enough to display selectivity. In contrast, in reactions where it is formed, tungstenocene almost always reacts with solvent [38]; it displays less discrimination (hence higher reactivity) than molybdenocene. The stability of higher oxidation states for third row metals relative to their second row analogues is quite consistent with this reasoning. Thus, reductive elimination from Mo(IV) is more facile than from W(IV).

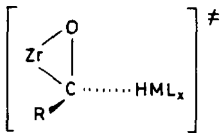
A number of other transition metal hydrides were screened for hydrogen transfer activity. Complex 2 was also found to react with $CpReH_4(PMe_2Ph)$. The products of this reaction, under one atm CO, were $Cp_2Zr(OEt)Me$ and the rhenium complex $CpReH_2(CO)(PMe_2Ph)$. No reaction was observed between 2 and $CpReH_2(CO)(PMe_2Ph)$. Likewise, $CpReH_4(PPh_3)$, $CpReH_2(PMe_2Ph)_2$, and $Cp_2W(H)Ph$ did not transfer hydride to the acyl ligand in 2.

The oxycarbene resonance form (Ib) shows clearly that the carbon of a η^2-acyl bound to a d^0 metal center should be quite electrophilic. In view of the fact that all hydride complexes successful in reducing these η^2-acyls possess filled and sterically accessible nonbonding d orbitals, we were attracted to a mechanism for all such reactions which is initiated by nucleophilic attack on the acyl carbon by a metal lone pair (eqn. 10).



(10)

This line of reasoning led us to examine Cp_2NbH_3, a d^0 complex, for hydrogen transfer to $Cp_2Zr[C(O)Me]Me$. If eqn. 10 accurately represents the initial interaction between the reactants, Cp_2NbH_3 should be an ineffective hydrogen transfer reagent. The observation that these complexes react readily to give $Cp_2Zr(OEt)Me$ and $Cp_2Nb(H)CO$ destroys the mechanistic proposal of eqn. 10, and brings us to the simpler mechanism of direct hydrogen transfer to the acyl carbon, by transition state III.



III

Conclusion

Dihapto zirconium acyls react smoothly with a number of transition metal hydrides. The ultimate products depend on the hydride used, with reduction of the acyl carbon (originally introduced as carbon monoxide) proceeding either to the olefinic or to the alcoholic oxidation level. The initial product can be viewed as insertion of a carbene carbon into a transition metal-hydrogen bond, but the mechanism is most consistent with direct attack by metal-bound hydrogen on the acyl carbon. This work represents the first detailed study of acyl group reduction utilizing transition metal hydrides that are only mildly hydridic. Although we were successful in demonstrating the reducing power of 'later' (ie.: Group VI) transition metal hydrides, all reactions reported here share the undesirable feature of forming Zr-0 bonds, *Catalytic* hydrogenation of CO will require a different strategy for activation of the CO moiety; we are therefore looking later in the transition series [39].

Acknowledgements

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25 Because of the facile carbonylation of Cp_2ZrMe_2 to Cp_2-Zr[C(O)Me]Me, hydrogen transfer reactions were often performed by treating a solution containing Cp_2ZrMe_2 and the metal hydride with one atm CO. We have established that the metal hydrides and metal alkyls employed here do not react with one another in the absence of CO at 25 “C.

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28 For all of the mixed metal dimers examined here, the Cp chemical shifts fall in distinct regions characteristic of coordination, in one case, to Mo or W and, in the other case, to the metal which supplied the hydride equivalents. We have not observed a case where these regions overlap significantly.

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