al–metal bonded M^{II}_2 state with metal-separated M^{III}_2, M = Rh or Ir), we have identified a transformation that results in a "boat":"chair" rearrangement.

Mononuclear (pentamethylcyclopentadienyl)(pyrazole) complexes of Rh and Ir have recently been prepared by us as well as by others.[6] Addition of NEt_3 to a solution in CH_2Cl_2 of orange $Rh(\eta^5\text{-}C_5Me_5)Cl_2(pzH)$ (**4**), followed by stirring (2 h), elution from a short alumina column using 20:1 CH_2Cl_2/MeOH, redissolution, and then precipitation with Et_2O afforded[7] $[Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}pz)]_2$ (**5**, 81% yield), the molecular geometry of which (as established[8] by using X-ray crystallography) is illustrated as Figure 1, top. After treatment of compound **5** with $AgBF_4$ in acetone solution, a white precipitate formed, which was removed by filtration; subsequent introduction of Et_2O by vapor diffusion led to crystallization (95%) of the known[6] dirhodium species $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}pz)_2(\mu\text{-}Cl)]BF_4$ (**6**), the cation geometry for which[9] possesses 2-fold symmetry and is shown in Figure 1, middle. During stirring (48 h) of an orange solution of compound **6** in MeOH with excess Zn dust and Cu sand (ca. 1:1), the mixture gradually turned black and then to a deep purple color: we attribute the latter to the dirhodium(II) complex $[Rh(\eta^5\text{-}C_5Me_5)(\mu\text{-}pz)]_2$ (**7**), although this product has not yet been isolated as a pure solid.

Starting from the precursor[10] $[Rh(\eta^5\text{-}C_5H_5)Cl_2]_2$, similar strategy afforded (55%) the analogue[11] $[Rh(\eta^5\text{-}C_5H_5)Cl(\mu\text{-}pz)]_2$ (**8**) of **5**, a methanolic solution of which when stirred with excess Zn dust underwent an abrupt color change from orange to purple after 30 min. Filtration, evacuation, then extraction into Et_2O led to recovery of the bright purple analogue $[Rh(\eta^5\text{-}C_5H_5)(\mu\text{-}pz)]_2$ (**9**) of **7**, which (unlike the latter) was obtained (ca. 20% yield) as crystals suitable for X-ray diffraction,[12] by sublimation in vacuo (95 °C): the molecular geometry is reproduced as Figure 1, bottom. Reaction of compound **9** with $NOBF_4$ results in reoxidation to a red, cationic dirhodium nitrosyl[13] $[Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}pz)_2(\mu\text{-}NO)]BF_4$ (**10**, 50%), while treatment with I_2 in Et_2O yields the diiodo analogue $[Rh(\eta^5\text{-}C_5H_5)I(\mu\text{-}pz)]_2$ (**11**, 71% yield) of **8**. Diiridium(III) analogues of compounds **5** and **6** have been isolated; reduction to a diiridium(II) species (cf. **7** or **9**) is being pursued.

Compound **5** adopts a rigorously centrosymmetric "chair" conformation (Figure 1) for the bridging unit (to our knowledge this is paralleled[14] in related chemistry only in two structures, those of $[Ti(\eta^5\text{-}C_5H_5)_2(\mu\text{-}pz)]_2$ and $[Rh(\eta^5\text{-}C_5H_5)pz(\mu\text{-}pz)]_2$), with the two Rh(III) centers 4.059 (2) Å apart; it is formally the dichlorine adduct of the dirhodium(II) complex **7** (cf. the relationship between **9** and **11**), which we anticipate will possess a metal–metal bonded geometry folded into a "boat" shape like that confirmed for **9** (Rh–Rh = 2.657 Å, Figure 1). This supposition is supported by the close similarity between the electronic absorption spectra of **7** and **9**, both of which contain low-energy maxima (respectively at 560, 502 nm) attributable to a $\sigma{:}\sigma^*$ transition from a Rh_2 bonding HOMO. The "chair":"boat" rearrangement is represented explicitly by chloride abstraction from **5** to give **6** (Figure 1), while the reverse conformational change is implicit in the **9**:**11** conversion (i.e., assuming **11** is structurally analogous to **5**). In crystals of complex **5** the pz heterocycles are within 1° of coplanarity, i.e., as they would be oriented in transition during ring inversion of the more familiar "boat" structures (vide supra). Such relationships imply that core conformational change is an energetically feasible mechanistic pathway in redox phenomena associated with **1**–**3** and could also be responsible for racemization of the inherently chiral molecular configuration[2] of **3**, thereby limiting stereochemical usefulness of the latter.

Acknowledgment. We thank the NSERC, Canada, for financial support including provision of a graduate fellowship (J.A.B.).

Supplementary Material Available: Listings of fractional atomic coordinates and isotropic temperature parameters, anisotropic temperature parameters, interatomic distances, and bond angles for **5**, **6**, and **9** (9 pages); listings of observed and calculated structure factors for **5**, **6**, and **9** (17 pages). Ordering information is given on any current masthead page.

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[7] Compound **5**. Anal. Calcd for $C_{26}H_{36}Cl_2N_4Rh_2$: C, 45.81; H, 5.29; N, 7.72. Found: C, 45.56; H, 5.28; N, 8.01. ^1H NMR (250 MHz, $CDCl_3$) δ 1.78 (s), 6.14 (t), 7.36 (d).

[8] Crystal data for compound **5**: $M = 798$; triclinic; space group $P\bar{1}$; $a = 8.785$ (2), $b = 10.469$ (4), $c = 8.675$ (2) Å; $\alpha = 79.34$ (2), $\beta = 80.43$ (2), $\gamma = 114.90$ (2)°; $V = 684$ (2) Å^3; $Z = 1$; $d_{calc} = 1.64$ g cm^{-3}; Mo Kα radiation, $\lambda = 0.71069$ Å; Nonius CAD4 diffractometer; 1348 reflections with $F_o^2 > 6\sigma(F_o^2)$ were used in the least-squares refinement to yield $R = 0.0602$, $R_w = 0.0644$.

[9] Crystal data for compound **6**: $M = 676.6$; monoclinic; space group $P2/n$; $a = 15.043$ (2), $b = 8.360$ (1), $c = 12.316$ (2) Å; $\beta = 110.58$ (2)°; $V = 1450.0$ (5) Å^3; $Z = 2$; $d_{calc} = 1.55$ g cm^{-3}; Mo Kα radiation, $\lambda = 0.71069$ Å; Nonius CAD4 diffractometer; 1676 reflections with $F_o^2 > 4\sigma(F_o^2)$ were used in the least-squares refinement to yield $R = 0.0507$, $R_w = 0.0519$.

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[11] Compound **8**. Anal. Calcd for $C_{16}H_{16}Cl_2N_4Rh_2$: C, 35.52; H, 2.98; N, 10.36; Cl, 13.11. Found: C, 35.58; H, 3.25; N, 9.92; Cl, 13.84. ^1H NMR (250 MHz, $CDCl_3$) δ 6.24 (s), 6.31 (t), 8.07 (d). Compound **9**. Anal. Calcd for $C_{16}H_{16}N_4Rh_2$: C, 40.88; H, 3.43; N, 11.91. Found: C, 40.96; H, 3.81; N, 11.15. ^1H NMR (250 MHz, $CDCl_3$) δ 5.29 (s), 5.90 (t), 7.32 (d). Compound **10**. Anal. Calcd for $C_{16}H_{16}BF_4N_5ORh_2$: C, 32.74; H, 2.75, N, 11.93. Found: C, 32.36; H, 2.91; N, 10.91. ^1H NMR (250 MHz, $CDCl_3$) δ 5.61 (s), 6.35 (t), 7.96 (d). Compound **11**. Anal. Calcd for $C_{16}H_{16}I_2N_4Rh_2$: C, 26.55; H, 2.23; N, 7.74. Found: C, 27.37; H, 2.98; N, 7.48. ^1H NMR (250 MHz, $CDCl_3$) δ 6.15 (s), 6.25 (t), 7.96 (d).

[12] Crystal data for compound **9**: $M = 470.1$; orthorhombic; space group $P2_12_12_1$; $a = 11.758$ (2), $b = 12.710$ (3), $c = 10.736$ (2) Å; $V = 1604.4$ (6) Å^3; $Z = 4$; $d_{calc} = 2.02$ g cm^{-3}; Mo Kα radiation, $\lambda = 0.71069$ Å; Nonius CAD4 diffractometer; 903 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the least-squares refinement to yield $R = 0.0799$, $R_w = 0.0791$.

[13] This complex has also been structurally characterized by single-crystal X-ray diffraction.

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Soluble Mono(pentamethylcyclopentadienyl)zirconium Hydrides: X-ray Structure of $(C_5Me_5)_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)$

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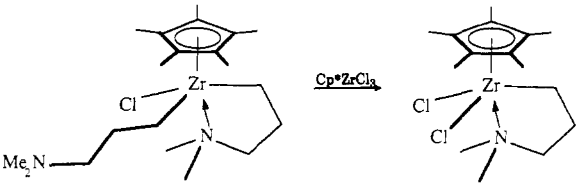
Summary: The 14-electron alkyl complex $Cp^*Zr[(CH_2)_3NMe_2]Cl_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$), containing a chelating (dimethylamino)propyl ligand, reacts with H_2 to form a soluble crystallizable mono-Cp* zirconium hydride with a complicated stoichiometry, tentatively formulated as "$Cp^*_3Zr_3H_4Cl_5$". Reaction of this compound with PMe_3 induces disproportionation, in which $Cp^*ZrCl_3(PMe_3)$ and $Cp^*_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)$, the first early-transition-metal (μ-H)$_3$-bridged dimer, are formed. An X-ray structure determination of this compound (space group $P2_1/c$, $a =$

15.599 (3) Å, b = 11.203 (3) Å, c = 16.862 (4) Å, β = 103.27 (2)° at 130 K, Z = 4) showed that one $Cp^*ZrCl(PMe_3)$– and one Cp^*ZrCl_2– moiety are bridged by three hydride ligands, with Zr–H distances ranging from 1.92 (3) to 2.35 (5) Å and Zr–H–Zr angles from 85.9 (17) to 104.1 (19)°.

Attempts to produce mono(pentamethylcyclopentadienyl)zirconium and hafnium hydrides by hydrogenolysis of $Cp^*M(alkyl)_nCl_{3-n}$ ($Cp^* = \eta^5\text{-}C_5Me_5$) have until now produced only insoluble polymeric products, even when a Lewis base is coordinated to the alkyl complex or excess Lewis base is added to the mixture.[1,2] The use of bulky phosphido ligands in the starting materials affords complexes such as $\{Cp^*Hf(R)[\mu\text{-}P(CMe_3)_2](\mu\text{-}H)\}_2$ (R = Cl, Me).[2] The isolation of soluble crystalline tetrameric $[Cp^*Hf(H)_2Cl]_4$ from hydrogenolysis of the diene complex Cp*Hf(2,3-dimethyl-1,3-butadiene)Cl was therefore remarkable.[3] Possibly the 2,3-dimethyl-2-butene produced in the hydrogenolysis initially remains coordinated to the hydrido species. This could prevent the hydride from polymerizing immediately and allow formation of well-defined crystallizable oligomers. This prompted us to study complexes containing Lewis base substituted alkyl ligands that can remain (weakly) bound to the metal after hydrogenolysis of the M–C bond. Here the synthesis of (dimethylamino)propyl complexes of zirconium is described, as well as their use as precursors for soluble Cp*Zr hydrides.

In the reaction of Cp^*ZrCl_3 with an excess of (dimethylamino)propyl Grignard reagent (0 °C), only two of the three chloride ligands are substituted to form the dialkyl monochloride complex $Cp^*Zr[(CH_2)_3NMe_2]_2Cl$ (**1**, eq 1). IR and low-temperature NMR spectroscopy[4] show that only one of the two dimethylamino groups is coordinated to the metal center at a time, indicating that **1** is sterically quite crowded. Comproportionation of **1** with Cp^*ZrCl_3 in toluene (20 °C) produces in good yield (84%) in the 14-electron monoalkyl complex $Cp^*Zr[(CH_2)_3NMe_2]Cl_2$ (**2**, eq 1), in which the amino group is coordinated to the metal center. In the ^1H NMR spectrum,[4] **2** shows a single resonance for the amino methyl groups, without coalescence broadening even down to −70 °C. This indicates either a very rapid rotation and inversion of the NMe_2-group on NMR time scale or a pseudo-trigonal-bipyramidal geometry of the complex.

$Cp^*ZrCl_3 + Me_2N(CH_2)_3MgCl$ (excess) →



1 2 (1)

Reaction of **2** with H_2 (1 atm, 20 °C) in aromatic solvents forms a clear yellow solution from which large yellow crystals can be obtained by diffusion of pentane into the mixture. Full characterization of this product was hampered by facile loss of cocrystallized solvent from the crystal lattice (making the material unsuitable for X-ray analysis). IR spectroscopy (ν_{Zr-H} = 1575, 1310, 1150, 901 cm^{-1}; ν_{Zr-D} = 1136, 975, 802, 636 cm^{-1} in the D_2 reaction product) does however indicate that a hydridic product has been formed. Low-temperature NMR spectroscopy[5] suggests a complicated stoichiometry, "$Cp^*_3Zr_3(H)_4Cl_5$" (**3**), with four nonequivalent hydrides and three nonequivalent Cp* ligands. Elemental analysis does not provide much of a clue to the nature of **3** because for crystalline material varying Zr:Cl ratios are found (from 1.7 to 2.0), probably due to varying amounts of cocrystallized Cp^*ZrCl_3 produced in the disproportionative formation of **3** (eq 2). Efforts to determine the structure of **3** are continuing.

$$\underset{\mathbf{2}}{Cp^*Zr[(CH_2)_3NMe_2]Cl_2} + H_2 \rightarrow$$

$$[Cp^*Zr(H)Cl_2{\cdot}NMe_2Pr] \xrightarrow[-Cp^*ZrCl_3]{-NMe_2Pr} \underset{\mathbf{3}}{\text{“}Cp^*_3Zr_3(H)_4Cl_5\text{”}} \quad (2)$$

Reaction of **3** with PMe_3 induces further disproportionation, forming a dinuclear hydrido complex, $Cp^*_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)$ (**4**) and $Cp^*ZrCl_3(PMe_3)$ (**5**, eq 3). The former can be obtained analytically pure as pale yellow crystals by slow crystallization from diethyl ether.

$$3\underset{\mathbf{3}}{\text{“}Cp^*_3Zr_3(H)_4Cl_5\text{”}} + 5PMe_3 \rightarrow$$

$$4\underset{\mathbf{4}}{Cp^*_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)} + \underset{\mathbf{5}}{Cp^*ZrCl_3(PMe_3)} \quad (3)$$

An X-ray structure determination[6] of **4** confirmed the triply hydride-bridged structure (Figure 1). It consists of one $Cp^*ZrCl(PMe_3)$ and one Cp^*ZrCl_2 moiety in nearly eclipsed conformation (torsion angles P(1)–Zr(1)–Zr(2)–Cl(3) = −11.34 (3)°, CT(1)–Zr(1)–Zr(2)–Cl(2) = 6.29 (3)°, Cl(1)–Zr(1)–Zr(2)–CT(2) = 28.38 (3)°; CT(x) is the Cp* centroid on Zr(x)), with three bridging hydrides staggered relative to the other ligands. The Zr(1)···Zr(2) distance of 3.126 (1) Å is considerably shorter than the 3.4599 (2) Å in the $(\mu\text{-}H)_2$ complex $[(\eta^5\text{-}C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$,[7] as is expected for a $(\mu\text{-}H)_3$ dimer.[8] The positions of the hydride ligands were determined unequivocally from the Fourier difference map and refined isotropically. The Zr–H distances to H(3) are longer than those for the other two H atoms, and the Zr(1)–H(3)–Zr(2) angle is very acute (85.9

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(4) **1**: ^1H NMR (300 MHz, toluene-d_8, −75 °C) δ 3.01 (s, 3 H, NMe), 2.4 (br m, 6 H, 3 CH_2), 2.22 (s, 6 H, NMe_2), 2.0 (br m, 2 H, CH_2), 1.88 (s, 15 H, Cp*), 1.83 (s, 3 H, NMe), 0.54 (br m, 2 H, $ZrCH_2$), −0.03 (br m, 1 H, Zr–CH*H*–). ^{13}C NMR (75.4 MHz, toluene-d_8, −65 °C): δ 12.28 (q, 126.2 Hz, Cp*–Me), 26.49 (t, 124.3 Hz, $-CH_2-$), 28.32 (t, 126.6 Hz, $-CH_2-$), 46.14 (q, 131.2 Hz, NMe_2), 49.38 (q, 131.1 Hz, NMe), 50.70 (q, 132.9 Hz, NMe), 51.94 (t, 120.3, Zr–CH_2), 59.95 (t, 128.9 Hz, Zr–CH_2), 63.29 (t, 128.9 Hz, N–CH_2), 67.57 (t, 136.4 Hz, N–CH_2), 119.74 (s, C_5Me_5). IR: ν_{CH} of noncoordinated NMe_2 at 2760 (mw) cm^{-1}. **2**: ^1H NMR (300 MHz, benzene-d_6, 20 °C) δ 2.67 (m, 2 H, NCH_2), 2.47 (s, 6 H, NMe_2), 1.91 (s, 15 H, Cp*), 1.80 (m, 2 H, CH_2), 0.69 (m, 2 H, $ZrCH_2$); ^{13}C NMR (75.4 MHz, benzene-d_6, 20 °C) δ 12.18 (q, 127.0 Hz, Cp*–Me), 26.73 (t, 126.6 Hz, CH_2), 48.03 (q, 137.0 Hz, NMe), 63.06 (t, 135.8 Hz, NCH_2), 65.23 (t, 116.8 Hz, $ZrCH_2$), 122.77 (s, C_5Me_5).

(5) **3**: ^1H NMR (300 MHz, toluene-d_8, −50 °C) δ 4.23 (1 H, H_A), 3.92 (1 H, H_B), 2.96 (1 H, H_C), 2.21 (s, 15 H, Cp*), 2.10 (s, 15 H, Cp*), 1.86 (s, 15 H, Cp*), 0.88 (1 H, H_D); hydride couplings J_{AB} = 9.9 Hz, J_{AC} = 10.6 Hz, J_{AD} = 3.3 Hz, J_{BC} = 0.0 Hz, J_{BD} = 6.2 Hz, J_{CD} = 1.5 Hz (determined by selective decoupling experiments). **4**: ^1H NMR (300 MHz, toluene-d_8, −30 °C) δ 4.73 (d, $^2J_{PH}$ = 12.1 Hz, t, $^2J_{HH}$ = 8 Hz, 1 H, μ-H), 4.44 (d, $^2J_{PH}$ = 18.3 Hz, t, $^2J_{HH}$ = 8 Hz, 1 H, μ-H), 2.97 (ps q, $^2J_{PH} \simeq {}^2J_{HH}$ = 8 Hz, 1 H, μ-H), 2.17 (s, 15 H, Cp*), 2.03 (s, 15 H, Cp*), 1.03 (d, $^2J_{PH}$ = 8.4 Hz, 3 H, PMe). At 75 °C only one μ-H resonance is observed at 4.09 ppm (br, 3 H); ^{31}P NMR (121.4 MHz, toluene-d_8, −30 °C, PMe_3 protons selectively decoupled) δ −18.1 (ddd, $^2J_{PH}$ = 18.3, 12.1, 8.3 Hz). At 75 °C a quartet is observed ($^2J_{PH}$ = 12.9 Hz).

(6) **4** crystallizes in the monoclinic space group $P2_1/c$ with a = 15.599 (3) Å, b = 11.203 (3) Å, c = 16.862 (4) Å, β = 103.27 (2)° (130 K), Z = 4. Reflections (5557) with $1.2 \le \theta \le 28°$ and $I \ge 2.5\sigma(I)$ were considered observed. All hydrogen atoms were located in the Fourier difference map and refined isotropically. R = 0.034, R_w = 0.039 ($w = [\sigma^2(F)]^{-1}$) for 432 refined parameters.

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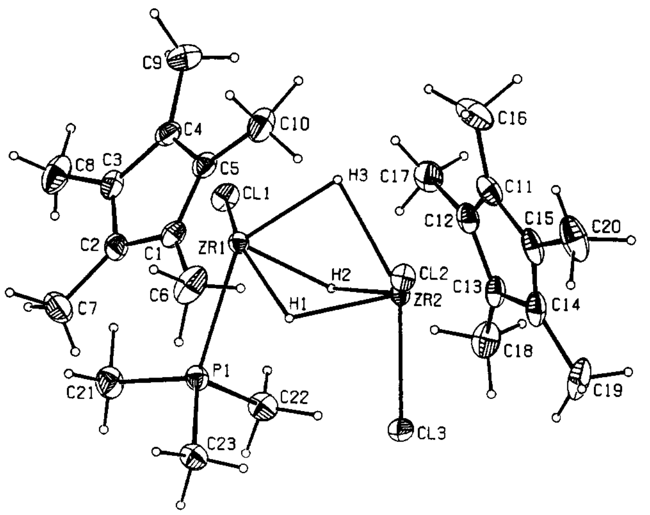

Figure 1. Molecular structure of $Cp^*_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)$ (4). Selected structural parameters are as follows: Zr(1)···Zr(2) = 3.126 (1), Zr(1)–Cl(1) = 2.470 (1), Zr(2)–Cl(2) = 2.456 (1), Zr(2)–Cl(3) = 2.452 (1), Zr(1)–P(1) = 2.744 (1), Zr(1)–H(1) = 1.92 (3), Zr(1)–H(2) = 2.00 (3), Zr(1)–H(3) = 2.24 (5), Zr(2)–H(1) = 2.04 (4), Zr(2)–H(2) = 1.98 (3), Zr(2)–H(3) = 2.35 (5) Å, ∠Zr(1)–H(1)–Zr(2) = 104.1 (19), ∠Zr(1)–H(2)–Zr(2) = 103.2 (14), ∠Zr(1)–H(3)–Zr(2) = 85.9 (17), ∠P(1)–Zr(1)–Cl(1) = 86.06 (3), ∠Cl(2)–Zr(2)–Cl(3) = 101.77 (3)°.

(2)°, compare Hf–H–Hf of 94 (5)° in $\{Cp^*Hf(Me)[\mu\text{-}P(CMe_3)_2](\mu\text{-}H)\}_2$[2]). At −30 °C the ^1H NMR spectrum[5] of 4 shows three nonequivalent hydride resonances, each with one $^2J_{PH}$ and two (equivalent) $^2J_{HH}$ couplings. At 75 °C all hydride signals are coalesced into one broad resonance, indicating rapid interchange of the hydrides at higher temperatures. Since at this temperature two different Cp* resonances remain, rapid exchange of Cl and PMe_3 between the metal centers apparently does not occur. Compound 4 is the first example of a $(\mu\text{-}H)_3$-bridged early-transition-metal dimer. In the heterobimetallic complex $Cp_2Zr(Cl)(H)_3Os(PMe_2Ph)_3$[9] the metal centers are probably also $(\mu\text{-}H)_3$ bridged, although the hydrides could not be located by X-ray diffraction. A number of late-transition-metal $(\mu\text{-}H)_3$ complexes are known (such as $[Fe_2(\mu\text{-}H)_3(triphos)_2][PF_6]$ and related compounds[10]).

Despite the difficulties encountered in the characterization of 3, the use of the (dimethylamino)propyl ligand has enabled us to obtain soluble, crystalline Cp*Zr hydrides. This makes it likely that intermediate stabilization of the newly formed hydride by an (already coordinated) weak Lewis base is essential to the formation of soluble complexes. For these sterically and electronically strongly unsaturated hydrides, the formation of thermodynamically favored oligomers with bridging hydride ligands is the driving force for the observed disproportionation to give complexes with complicated stoichiometries. Bercaw et al. already observed that in the hydrogenolysis of $Cp^*Hf[P(CMe_3)_2]Cl_2$ an intermediate $Cp^*Hf(H)Cl_2$ species can be trapped with ethene[2] but in the absence of trapping agents probably disproportionates. This contrasts with the behavior of (sterically more encumbered) monomeric electron-deficient complexes, where the thermodynamic bias toward dispersion of π-donor ligands (like halides or alkoxides) promotes comproportionation rather than disproportionation.[11] Presently we are investigating a range of Cp*M hydrides (M = Zr, Hf) with varying stoichiometries and their interaction with Lewis bases to get a more complete view of the structure-determining factors in strongly electron-deficient early-transition-metal hydrides.

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Supplementary Material Available: Experimental details, spectral and analytical data for all compounds, details of structure determination, crystal data, and lists of positional and thermal parameters for 4 (15 pages); a listing of observed and calculated structure factors for 4 (26 pages). Ordering information is given on any current masthead page.

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First Prototype of Neutral Diacyl Complexes of Platinum(II) and Related Acyl(alkyl) Complexes of Platinum(II)

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Summary: The acyl(carbonyl) complex *cis*-$[Pt(COPh)(CO)(PPh_3)_2]^+$ (**2a**) reacts with PhLi to yield the neutral dibenzoyl complex *cis*-$Pt(COPh)_2(PPh_3)_2$ (**3a**) in 34% isolated yield. The crystallographic data of **3a** indicate that it is disposed in a distorted square-planar geometry with two benzoyl carbonyls in the s-trans configuration. The analogous reaction of the cationic **2a** with MeLi, however, gives three products: *cis*-$Pt(COPh)(COMe)(PPh_3)_2$ (**3b**), *cis*-$Pt(COPh)(Me)(PPh_3)_2$ (**4**), and $Pt(COPh)(Me)(CO)(PPh_3)$ (**5a**) in a relative ratio of 1:2.5:3 in 55% total yield. In a similar reaction carried out in the presence of extra PPh_3, only **3b** and **4** were obtained, in a 1:3.5 ratio in 90% total yield. The structures of the complexes **4** and **5a** were determined by X-ray crystallography, and both are square planar. In **5a**, the PPh_3 was found trans to the benzoyl ligand. The replacement of a PPh_3 in **4** by CO gives **5a** and its regio isomer **5b**, whose PPh_3 is instead trans to the methyl group. The complex **5b** is kinetically favored but thermodynamically unstable. These substitution reactions are reversible with the equilibria in favor of **4**.

The rare diacyl complexes of the prototype RC(O)MC(O)R′ (wherein R and R′ are hydrocarbyls) are either anionic[1,2] or are stabilized by bridging structures.[2-4] Curi-

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