

# New Sandwich Complexes Containing 6,6-Dimethylcyclohexadienyl (dmCh): (dmCh)<sub>2</sub>M (M = Ti, V, Cr, Fe) and (dmCh)<sub>2</sub>M-CO (M = Ti, V)

Peter T. DiMauro and Peter T. Wolczanski\*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853

Received August 14, 1986

Deprotonation of 5,5-dimethylcyclohexadiene ((dmCh)H) with KO-*t*-Bu/*n*-BuLi afforded potassium 6,6-dimethylcyclohexadienyl (K(dmCh)). Treatment of MCl<sub>n</sub>(THF)<sub>m</sub> with *n* equiv of K(dmCh) afforded the new sandwich complexes (dmCh)<sub>2</sub>M (M = Ti (1), V (2), Cr (3), Fe (5)) in moderate yield (35-68%). The Ti and Fe complexes are diamagnetic, while 2 and 3 possess one and two unpaired electrons. When exposed to CO, 1 and 2 formed the monocarbonyl adducts (dmCh)<sub>2</sub>M-CO (M = Ti (6), V (7)); EPR spectra of thermally unstable (dmCh)<sub>2</sub>V-PMe<sub>3</sub> (8) and (dmCh)<sub>2</sub>V-PF<sub>3</sub> (10) and NMR evidence for (dmCh)<sub>2</sub>Ti-PF<sub>3</sub> (9) were also obtained. While Ch<sub>2</sub>Fe (11, Ch = η<sup>5</sup>-C<sub>6</sub>H<sub>7</sub>) could be prepared from FeCl<sub>2</sub> and LiCh, generated via LDA and 1,4-C<sub>6</sub>H<sub>8</sub> (-78 °C), this procedure was not general. The isomerization of 11 to (η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)-Fe(η<sup>4</sup>-1,3-C<sub>6</sub>H<sub>8</sub>) (12), concomitant with Fe<sup>0</sup>, was also noted. The expected C<sub>2v</sub> symmetry of 6 was confirmed via an X-ray crystallographic investigation. Crystal data: monoclinic, P<sub>2</sub><sub>1</sub>/n, *a* = 7.372 (1) Å, *b* = 9.900 (1) Å, *c* = 22.101 (3) Å, β = 105.100 (8)°, *Z* = 4, *T* = 25 °C. Standard refinement procedures yielded an *R* of 0.074 and *R<sub>w</sub>* = 0.076 from 1356 reflections where |*F<sub>o</sub>*| ≥ 3σ(*F<sub>o</sub>*). The structures, bonding, and stability of 1-10 are discussed in relation to Cp and pentadienyl analogues.

## Introduction

The synthesis and reactivity of complexes containing the ubiquitous cyclopentadienyl (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) ligand have commanded the attention of organometallic chemists for over three decades.<sup>1</sup> Similarly π-bonded hydrocarbon ligands, such as allyl and arene, have also undergone extensive investigation.<sup>1,2</sup> Until recently, acyclic pentadienyl<sup>3</sup> analogues to Cp had not been fully exploited. Seminal work by Ernst et al.<sup>4,5</sup> has shown that η<sup>5</sup>-C<sub>5</sub>H<sub>7</sub> (pd) and various alkylated congeners are versatile ligands possessing features related to both Cp and/or allyl.<sup>3</sup> Several available mononuclear (U, W, and S)<sup>3,6</sup> and binuclear<sup>7</sup> bonding modes in combination with potential η<sup>5</sup>-η<sup>3</sup>-η<sup>1</sup> lability render the pd ligand attractive from the standpoint of reactivity. Favorable energetics, in conjunction with a relatively small HOMO-LUMO gap, enable pentadienyl ligands to impart a strong ligand field.<sup>8,9</sup> These ligands also wrap efficiently about a metal center to obtain excellent orbital overlap.<sup>3</sup> As a result, unusual, coordinatively unsaturated, divalent sandwich complexes, termed "open metallocenes", of Ti,<sup>10</sup> V, Cr,<sup>11</sup> Zr, and Nb<sup>6</sup> have been prepared. In certain cases, the bound pentadienyl displays

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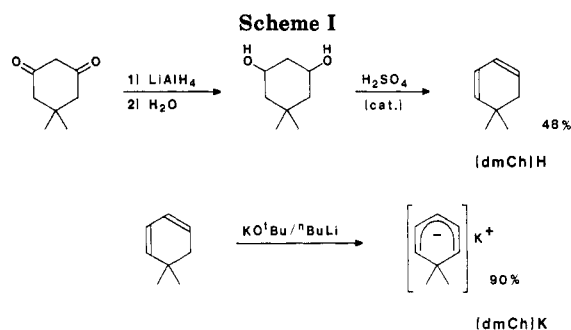
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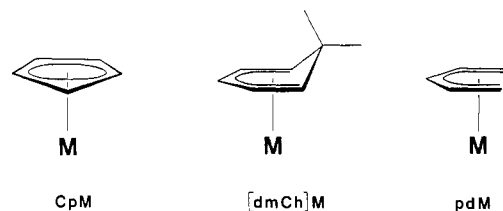
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reactivity akin to a radical by coupling to form a bridging tetraene ligand.<sup>12</sup> In other instances, the transformations and bonding of pd ligands correspond with metal-alkyl behavior; CO insertion<sup>13</sup> and η<sup>5</sup>:η<sup>1</sup>-bridges<sup>7</sup> have been observed.

Described herein is a new class of sandwich complexes based on the 6,6-dimethylcyclohexadienyl (η<sup>5</sup>-6,6-Me<sub>2</sub>C<sub>6</sub>H<sub>5</sub> = dmCh) ligand.



This dienyl ligand type was viewed as bridging the gap between Cp and the assorted acyclic pentadienyl species. It was expected that the envelope conformation of the C<sub>6</sub> ring would direct the p orbitals of the dienyl toward the metal, thus engendering strong overlap. Orbital energetics similar to the pd systems would help create a strong ligand field, but the cyclic nature of the ligand would diminish its ability to wrap about the metal. In addition, steric

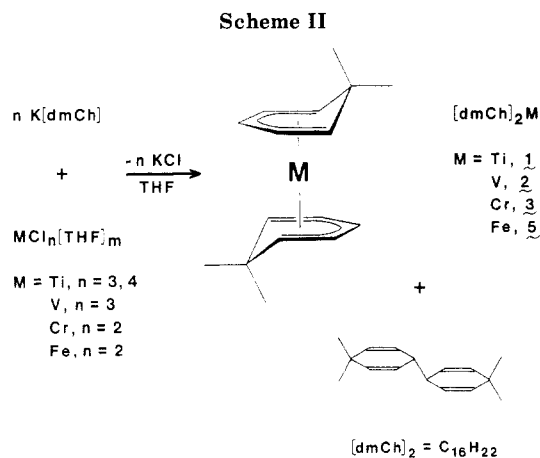
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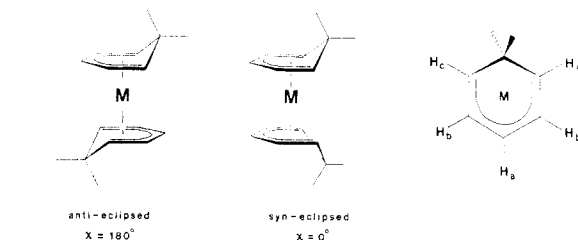


properties of the *gem*-dimethyl section would discourage reactivity at the 1- and 5-positions of the ring, allowing dmCh to function in an ancillary manner. From these synthetic, spectroscopic, and structural studies, the above qualities are indeed apparent.

### Synthesis and Characterization

**Ligand Synthesis.** The utilization of cyclohexadienyl ligands has been hampered by the lack of general preparative methodology. Metathetical routes using  $[\text{C}_6\text{H}_7]\text{M}'$  ( $\text{M}' = \text{Li}, \text{Na}, \text{K}$ ) are problematic due to the instability of the anion relative to benzene and  $\text{M}'\text{H}$  (vide infra).<sup>14</sup> Attack of (arene) $\text{ML}_n$  complexes by alkyl anions is successful if L is sufficiently electron-withdrawing.<sup>15</sup> Methods employing  $\text{R}^-$  or  $\text{H}^-$  addition to  $[(\text{arene})\text{ML}_n]^+$  complexes<sup>16</sup> are often effective, but complications sometimes arise.<sup>17,18</sup> For example, Wilkinson initially prepared  $\text{Ch}_2\text{Ru}$  ( $\text{Ch} = \eta^5\text{-C}_6\text{H}_7$ ) via  $\text{LiAlH}_4$  reduction of  $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}]^{2+}$ , but a substantial amount of  $(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-1,3-C}_6\text{H}_8)\text{Ru}$  was also produced.<sup>19</sup> Fortunately, anions derived from 5,5-dialkylcyclohexadienes are stable and thus suitable for metathetical procedures.<sup>14</sup>

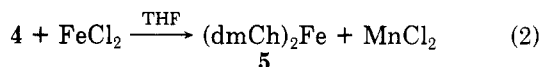
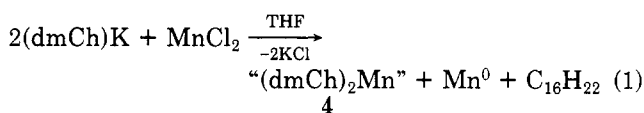
The synthesis of 5,5-dimethylcyclohexadiene (dmCh)H was accomplished through slight modification of Walling's method,<sup>20</sup> as illustrated in Scheme I. Reduction of dimedone with  $\text{LiAlH}_4$  provided 5,5-dimethylcyclohexane-1,3-diol which was subsequently dehydrated with  $\text{H}_2\text{SO}_4$  to obtain the desired diene (48% overall). An alternate method employing condensation of methyl vinyl ketone with  $\text{R}_2\text{CCHO}$  to give 4,4-dialkyl-2-cyclohexenone, followed by Shapiro olefination<sup>21</sup> of the corresponding tosylhydrazone, was also explored. Although this method is more versatile, since a variety of 5,5-dialkylcyclohexadienes may be synthesized, product purification



**Figure 1.** Possible dmCh orientations. The angle  $\chi$  refers to an oscillation of the bottom dmCh relative to the top ligand. If  $\chi = 60$  or  $120^\circ$ , the orientation is considered gauche-eclipsed. Any other  $\chi$  value is considered staggered.

proved laborious and the procedure was generally less applicable to large scales. Deprotonation of (dmCh)H with Schlosser's base<sup>22</sup> afforded the potassium anion  $(\text{dmCh})\text{K}^{23}$  as a pyrophoric yellow solid in excellent yield (90%). Other anionic species (i.e.,  $(\text{dmCh})\text{MgCl}$ ,  $(\text{dmCh})_2\text{Zn}$ ) tested held little or no advantage over  $(\text{dmCh})\text{K}$ , from which they were derived.

**Preparation of  $(\text{dmCh})_2\text{M}$  Complexes.** Scheme II indicates a generic equation for the formation of  $(\text{dmCh})_2\text{M}$  ( $\text{M} = \text{Ti}$  (1),  $\text{V}$  (2),  $\text{Cr}$  (3),  $\text{Fe}$  (5)) complexes. Metal chloride THF adducts<sup>24</sup> were found helpful in purifying and solubilizing  $\text{MX}_n$  precursors. The coupled ligand dimer  $(\text{dmCh})_2$  was produced as a byproduct due to reduction of the precursor halide. While no attempts to quantify the amount of this impurity were made, the moderate yields of 1–3 and 5 (35–68%) suggested that significant reduction was occurring beyond that implied by the stoichiometries. Formation of the deep pink-red  $(\text{dmCh})_2\text{Mn}^+$  (4, ~15%) was accompanied by substantial amounts of Mn metal and the  $\text{C}_{16}\text{H}_{22}$  byproduct (eq 1).



Attempts at separating paramagnetic 4 from the latter were ineffective. The conversion of 4 to  $(\text{dmCh})_2\text{Fe}$  (5) upon addition of  $\text{FeCl}_2$  implied a similar structure (eq 2); however, a species analogous to Ernst's  $(3\text{-MeC}_5\text{H}_6)_4\text{Mn}_3$  complex<sup>7</sup> might also serve to transfer dmCh. While crimson  $(\text{dmCh})_2\text{Cr}$  (3) could be purified by sublimation and 5 via crystallization from pentane, the presence of  $(\text{dmCh})_2$  proved deleterious to the isolation of forest-green  $(\text{dmCh})_2\text{Ti}$  (1) and scarlet  $(\text{dmCh})_2\text{V}$  (2). These highly soluble organometallics could not be crystallized in the presence of the organic oil, the volatility of which was commensurate with the complexes. Purification of 1 and 2 was accomplished through decomposition of their respective CO and  $\text{PMe}_3$  adducts (vide infra).

Paramagnetic  $(\text{dmCh})_2\text{V}$  (2) and  $(\text{dmCh})_2\text{Cr}$  (3) possess near spin-only solution magnetic moments of 2.1 and 2.6  $\mu_B$ ,<sup>25</sup> respectively (Table I). The 25 °C solution  $(\text{C}_7\text{H}_8)$  EPR spectrum of 2 consisted of an eight-line pattern ( $\langle g \rangle = 1.9925$ ,  $a(^{51}\text{V}) = 54 \text{ G}$ ) which exhibited little anisotropy when cooled to 10 K. Diamagnetic  $(\text{dmCh})_2\text{Ti}$  (1) and  $(\text{dmCh})_2\text{Fe}$  (5) exhibited three types of di-

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Table I. NMR (<sup>1</sup>H, <sup>13</sup>C), EPR, IR, and Magnetic Data for (dmCh)<sub>2</sub>M and (dmCh)<sub>2</sub>M-L Complexes (dmCh = η<sup>5</sup>-H<sub>a</sub>C(CH<sub>b</sub>)(CH<sub>c</sub>)(CMe<sub>2</sub>)(CH<sub>c</sub>')(CH<sub>b</sub>'))

compd, IR (cm <sup>-1</sup> ) <sup>a</sup>	<sup>1</sup> H NMR δ (J, Hz)	<sup>13</sup> C NMR δ <sup>b</sup>	
(dmCh) <sub>2</sub> Ti (1) <sup>c</sup>	50 °C <sup>d</sup>	-0.46 (s, Me (exo), 6 H)	28.10 (Me)
		1.02 (s, Me (endo), 6 H)	28.68 (Me)
		3.87 (dd, H <sub>c,c'</sub> , 4 H, J = 8, 2)	93.97 (C(1,5))
		5.54 (tt, H <sub>a</sub> , 2 H, J = 8, 2)	105.9 (C(3))
		6.04 (*t, H <sub>b,b'</sub> , 4 H, J = 8)	110.5 (C(2,4))
	-87 °C <sup>d</sup>	-0.47 (s, Me (exo), 6 H)	
		1.09 (s, Me (endo), 6 H)	
		2.29 (d, H <sub>c</sub> , J = 7.7, 2 H)	
		5.25 (*t, H <sub>b</sub> , J = 7.7, 2 H)	
		5.50 (m, H <sub>a</sub> , H <sub>c'</sub> , 4 H)	
(dmCh) <sub>2</sub> Fe (5) <sup>b</sup>		6.83 (*t, H <sub>b</sub> , J = 7.7, 2 H)	
		0.35 (s, Me (exo), 6 H)	30.54 (Me)
		1.55 (s, Me (endo), 6 H)	33.36 (Me)
		2.68 (dd, H <sub>c,c'</sub> , 4 H, J = 6.2, 1)	33.56 (CMe <sub>2</sub> )
		3.97 (*t, H <sub>b,b'</sub> , 4 H, J = 6.2, 5.2)	48.87 (C(1,5))
		4.72 (tt, H <sub>a</sub> , 2 H, J = 5.2, 1)	77.88 (C(3))
(dmCh) <sub>2</sub> Ti-CO (6) <sup>b,c</sup> ν(CO) = 1904		83.58 (C(2,4))	
		1.03 (s, Me (exo), 6 H)	28.44 (Me)
		1.91 (s, Me (endo), 6 H)	30.78 (Me)
		3.35 (dd, H <sub>b,b'</sub> , 4 H, J = 7, 8)	77.24 (C(1,5))
		4.26 (dd, H <sub>c,c'</sub> , 4 H, J = 8, 1)	93.06 (C(3))
(dmCh) <sub>2</sub> TiPF <sub>3</sub> (9)		4.84 (tt, H <sub>a</sub> , 2 H, J = 7, 1)	108.1 (C(2,4))
	-80 °C <sup>e</sup>	0.58 (s, Me (exo), 6 H)	269.7 (CO)
		0.75 (s, Me (endo), 6 H)	
		3.12 (br m, H <sub>b,b'</sub> , 4 H)	
	4.41 (br m, H <sub>c,c'</sub> , 4 H)		
	4.69 (br m, H <sub>a</sub> , 2 H)		
compd, <sup>a</sup> IR (cm <sup>-1</sup> )	μ, <sup>f</sup> μ <sub>B</sub>	⟨g⟩	
(dmCh) <sub>2</sub> V (2)	2.1 <sup>b</sup>	1.9925	a( <sup>51</sup> V) = 54 G
(dmCh) <sub>2</sub> Cr (3)	2.6 <sup>d</sup>		
(dmCh) <sub>2</sub> V-CO (7) ν(CO) = 1912	2.0 <sup>d</sup>	1.984	a( <sup>51</sup> V) = 71 G
(dmCh) <sub>2</sub> V-PMe <sub>3</sub> (8)	-90 °C	1.99	a( <sup>13</sup> CO) ≈ 8 G a( <sup>51</sup> V) = 76 G a( <sup>31</sup> P) < 6 G
(dmCh) <sub>2</sub> V-PF <sub>3</sub> (10)	-80 °C	1.99	a( <sup>51</sup> V) = 79 G a( <sup>31</sup> P) < 6 G

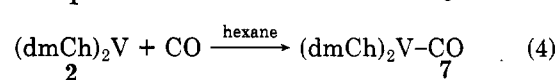
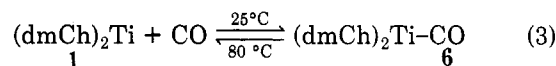
<sup>a</sup> IR in cyclohexane solution. <sup>b</sup> Benzene-d<sub>6</sub>, referenced to Me<sub>4</sub>Si at δ 0.00 or C<sub>6</sub>D<sub>6</sub> at δ 128.00 (25 °C). <sup>c</sup> Quaternary carbon not located. <sup>d</sup> Toluene-d<sub>8</sub>, referenced to Me<sub>4</sub>Si at δ 0.00. <sup>e</sup> Broad due to PF<sub>3</sub> dissociation. <sup>f</sup> Evans method.<sup>25</sup>

methylcyclohexadienyl ring hydrogens (1:2:2) in addition to two Me resonances at 25 °C. At low-temperature (-87 °C), the apparent C<sub>2h</sub> (anti-eclipsed, χ = 180°, Figure 1)

or C<sub>2v</sub> (syn-eclipsed, χ = 0°) symmetry of 1 was lowered to C<sub>2</sub>, as evidenced by the appearance of a new set of five inequivalent ring hydrogens, implicating equivalent dmCh ligands oriented in a gauche (0° < χ < 180°) fashion. From coalescence measurements (T<sub>c</sub> = -25 °C for H<sub>b</sub>H<sub>b'</sub>; T<sub>c</sub> = -20 °C for H<sub>c</sub>H<sub>c'</sub>), the barrier to cyclohexadienyl oscillation is 10.8 ± 0.5 kcal/mol.<sup>26</sup>

The early-metal derivatives are highly sensitive, immediately turning black and amorphous upon exposure to air, yet possess remarkable thermal stabilities. In benzene solution, 1, 2, and 3 may be heated at 75 °C for 1 week without noticeable decomposition. At 120 °C, (dmCh)<sub>2</sub>Ti (1) rapidly degraded (30 min) to yield toluene (~60%) as the only identifiable product. Thermolysis of 1 in the presence of a 20-fold excess of PMe<sub>3</sub> again resulted in the formation of toluene (~60%), but under somewhat milder conditions (60 °C, 1 week). While the pathway for the formal loss of Me<sup>-</sup> from dmCh is unknown, a similar degradation of (dmCh)K to yield toluene occurs at 80 °C. It is conceivable that the decomposition of 1 is initiated by a β-Me migration<sup>27</sup> from the dmCh to Ti, perhaps via η<sup>3</sup> or η<sup>1</sup>-coordination, given the slight rate acceleration when PMe<sub>3</sub> is present. Brookhart<sup>28</sup> has observed the reverse of this process, the migration of a Me to a coordinated arene. The Ti complex did not react with H<sub>2</sub>, CH<sub>3</sub>I, AlMe<sub>3</sub>, or Ph<sub>3</sub>P=CH<sub>2</sub> at 25 °C; subsequent heating resulted in decomposition. Air-stable, 18-electron (dmCh)<sub>2</sub>Fe (5) was stable for 8 days at 100 °C and degraded only slightly at 150 °C (2 h), forming Fe metal.

**Adduct Formation.** Monocarbonyl adducts of the Ti and V complexes were prepared by exposing hexane solutions of 1 and 2 to 1 atm of CO (eq 3 and 4). Red-orange



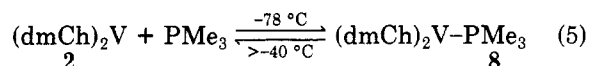
(dmCh)<sub>2</sub>Ti-CO (6) was formed quantitatively (<sup>1</sup>H NMR). Yellow-green needlelike crystals of (dmCh)<sub>2</sub>V-CO (7), obtained from a brown solution, appeared isomorphous to those of the Ti analogue. When the paramagnetic V monocarbonyl (μ = 2.0 μ<sub>B</sub>) was prepared with <sup>13</sup>C (<sup>7</sup>-<sup>13</sup>C), an EPR spectrum (⟨g⟩ = 1.984) displaying hyperfine coupling to both <sup>51</sup>V (a = 71 G) and <sup>13</sup>C (a ≈ 8 G) was observed. The reversible carbonylation of (dmCh)<sub>2</sub>Ti (1) provided the means by which crystalline, analytically pure samples of this 14-electron complex could be obtained. The Ti monocarbonyl 6 could be crystallized and washed free of impurity (dmCh)<sub>2</sub>, present in the crude precursor. Repeated thermolysis (80 °C) and CO removal from a toluene solution of 6 in vacuo resulted in solid 1, which could be sublimed (25 °C, 10<sup>-4</sup> torr) to purity. The V monocarbonyl 7 could be similarly heated for 18 days without change. While 7 was also stable in the solid state, 6 surprisingly degraded to an amorphous black solid (2 weeks, 25 °C) and was therefore stored at -20 °C.

Treatment of 2 with excess PMe<sub>3</sub> at -78 °C in pentane resulted in a red-brown precipitate, formulated as (dmCh)<sub>2</sub>V-PMe<sub>3</sub> (8) according to eq 5. The PMe<sub>3</sub> adduct 8 proved useful in purifying its precursor, crude (dmCh)<sub>2</sub>V

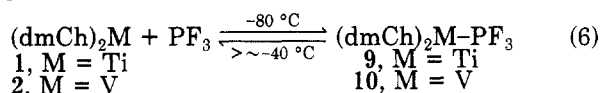
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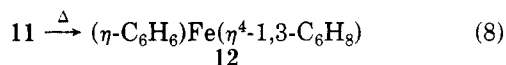
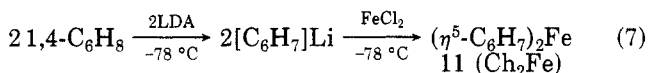


(2). Repeated cold washing of precipitated 8 ( $-78\text{ }^\circ\text{C}$ ) with pentane, followed by warming, loss of  $\text{PMe}_3$ , and subsequent sublimation ( $25\text{ }^\circ\text{C}$ ,  $10^{-4}$  torr) afforded analytically pure 2. The toluene-soluble phosphine adduct 8 was characterized by an 8-line EPR pattern ( $\langle g \rangle = 1.99$ ,  $a(^{51}\text{V}) = 76\text{ G}$ ) at  $-90\text{ }^\circ\text{C}$ .<sup>29</sup> No hyperfine interaction due to phosphorus could be detected, suggesting that any coupling must be less than the observed line widths ( $\sim 6\text{ G}$ ). Alternatively,  $\text{PMe}_3$  may be a sufficiently good nucleophile to attack the unencumbered 3-position of a dmCh ligand,<sup>30</sup> resulting in a zwitterionic, formally low-spin  $d^5$  15-electron complex, ( $\eta^4$ -6,6-dimethyl-(3- $\text{PMe}_3$ )-1,4-cyclohexadiene)-(dmCh)V (8'), also consistent with the EPR spectrum. The former 17-electron structure 8 is favored for the following reasons: (1) the  $^{51}\text{V}$  hyperfine coupling is near that of 7; (2) the comparable  $^{13}\text{C}$  hyperfine of 7- $^{13}\text{C}$  is also small; (3) analogous (pd) $_2\text{V}-\text{PR}_3$  species have variable  $^{31}\text{P}$  hyperfine couplings;<sup>31</sup> (4) the structurally characterized, low-spin ( $\eta^5$ -2,4- $\text{C}_7\text{H}_{11}$ ) $_2\text{Nb}-\text{PET}_3$  complex manifests no phosphorus coupling;<sup>6</sup> (5)  $\text{PF}_3$ , a poor nucleophile, also formed a low-temperature ( $-80\text{ }^\circ\text{C}$ ) adduct,  $(\text{dmCh})_2\text{V}-\text{PF}_3$  (10, eq 6),



which exhibited an 8-line EPR pattern ( $\langle g \rangle = 1.99$ ,  $a(^{51}\text{V}) = 79\text{ G}$ ) with no observable  $^{31}\text{P}$ -coupling; (6) all indications are that corresponding Ti-phosphine species are simple adducts. At  $-80\text{ }^\circ\text{C}$ , the  $^1\text{H}$  NMR spectrum of red  $(\text{dmCh})_2\text{Ti}-\text{PF}_3$  (9) is slightly broadened due to dissociation, yet the spectrum is clearly consistent with a donor complex akin to 7. Both  $\text{PMe}_3$  and  $\text{P(OMe)}_3$  appeared to bind to  $(\text{dmCh})_2\text{Ti}$  (1) at  $-78\text{ }^\circ\text{C}$ , as indicated by a color change (green to red-brown), but the lability of these species obviated direct characterization.

With the dmCh derivatives providing precedence, metathetical routes to the parent cyclohexadienyl complexes were undertaken. Unfortunately, the aforementioned instability of the cyclohexadienyl anion<sup>14</sup> proved to be an insurmountable barrier for every metal except iron. Treatment of 1,4-cyclohexadiene (1,4- $\text{C}_6\text{H}_8$ ) with LDA at  $-78\text{ }^\circ\text{C}$  resulted in a deep yellow-orange solution, indicative of  $\text{C}_6\text{H}_7\text{-Li}$ .<sup>14</sup> Subsequent addition of  $\text{FeCl}_2$  resulted in the formation of thermally unstable  $\text{Ch}_2\text{Fe}$  (11, 46%, eq 7).



Thermolysis of 11 ( $80\text{ }^\circ\text{C}$ , 2 h) afforded  $(\eta^6\text{-}\text{C}_6\text{H}_6)\text{Fe}(\eta^4\text{-}1,3\text{-}\text{C}_6\text{H}_8)$  (12, eq 8)<sup>32</sup> concomitant with  $\text{Fe}^0$ . Similar treatments other metal halides generated reduction products,  $\text{M}^0$  and  $(\text{dmCh})_2$ :  $(\eta^6\text{-}\text{C}_6\text{H}_6)_2\text{Cr}$  was formed from  $\text{CrCl}_2(\text{THF})_2$  and 2 equiv of  $\text{ChLi}$  in reasonable yield (68%).

(29) At temperatures  $>-90\text{ }^\circ\text{C}$ , signals attributable to 2 begin to appear.

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Table II. Selected Interatomic Distances (Å) and Angles (deg) for  $(\text{dmCh})_2\text{Ti}-\text{CO}$  (6)

Interatomic Distances <sup>a</sup>			
Ti-C1	1.978 (9)	C4-C6	1.397 (10)
C1-O1	1.168 (9)	C6-C7	1.530 (10)
Ti-C2	2.298 (10)	C5...C6	2.412 (10)
Ti-C3	2.301 (7)	C10-C12	1.421 (13)
Ti-C4	2.278 (10)	C12-C14	1.391 (12)
Ti-C5	2.386 (7)	C14-C15	1.547 (11)
Ti-C6	2.390 (8)	C10-C11	1.444 (11)
Ti-C10	2.301 (8)	C11-C13	1.394 (11)
Ti-C11	2.298 (10)	C13-C15	1.543 (11)
Ti-C12	2.281 (7)	C13...C14	2.401 (11)
Ti-C13	2.377 (7)	C7-C8	1.541 (11)
Ti-C14	2.409 (7)	C7-C9	1.567 (10)
C2-C3	1.427 (10)	C15-C16	1.532 (12)
C3-C5	1.388 (10)	C15-C17	1.551 (12)
C5-C7	1.546 (11)	Ti-R1	1.925
C2-C4	1.426 (12)	Ti-R2	1.902

Interatomic Angles			
Ti-C1-O1	178.8 (7)	C13-Ti-C14	60.2 (3)
R1-Ti-R2	155	C3-C2-C4	118.0 (6)
C2-Ti-C10	84.2 (3)	C11-C10-C12	116.6 (7)
C3-Ti-C11	92.9 (3)	C2-C3-C5	119.9 (8)
C4-Ti-C12	95.1 (3)	C10-C11-C13	119.0 (8)
C5-Ti-C13	115.6 (2)	C2-C4-C6	120.4 (6)
C6-Ti-C14	117.2 (3)	C10-C12-C14	122.6 (7)
C2-Ti-C3	36.1 (2)	C3-C5-C7	116.9 (6)
C2-Ti-C4	36.3 (4)	C11-C13-C15	118.2 (6)
C10-Ti-C11	36.6 (3)	C4-C6-C7	116.7 (7)
C10-Ti-C12	36.1 (3)	C12-C14-C15	115.8 (8)
C3-Ti-C5	34.4 (2)	C5-C7-C6	103.3 (6)
C4-Ti-C6	34.7 (2)	C13-C15-C14	101.9 (6)
C11-Ti-C13	34.6 (3)	C8-C7-C9	107.2 (6)
C12-Ti-C14	34.4 (3)	C16-C15-C17	109.3 (6)
C5-Ti-C6	60.6 (2)		

<sup>a</sup>R1 is defined as the centroid of the triangle C2,C5,C6; R2 is defined as the centroid of the triangle C10,C13,C14. The distance of the normal (C2,C5,C6 plane) to the Ti is 1.921 Å; (C10,C13,C14 plane), 1.902 Å.

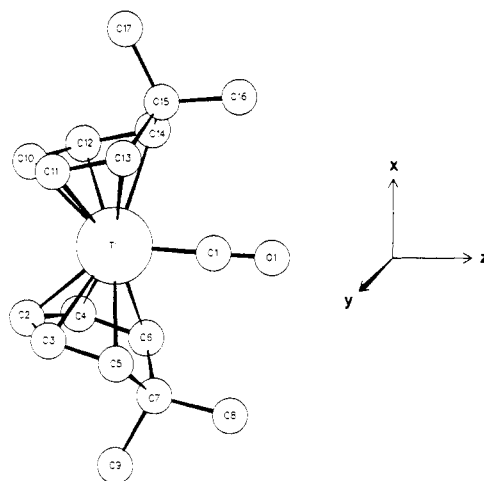


Figure 2. Molecular structure of  $(\text{dmCh})_2\text{Ti}-\text{CO}$  (6).

**Molecular Structure of  $(\text{dmCh})_2\text{Ti}-\text{CO}$  (6).** A single-crystal X-ray structure determination (monoclinic,  $P2_1/n$ ) confirmed the expected syn-eclipsed conformation of the dmCh units and overall near  $C_{2v}$  geometry of 6 (Figure 2, Table II). The symmetry is not crystallographically imposed; thus the top dmCh is twisted slightly ( $<1^\circ$ ) relative to its counterpart. The envelope angle of each ring, relative to the plane of bonded atoms, is  $46^\circ$ . Each dmCh is tipped away from the Ti at the 1- and 5-positions (C5,6,13,14). The bound carbons in each ring are nearly coplanar (C2-6 plane,  $\sum\sigma^2 = 0.002\text{ \AA}^2$ ; C10-14 plane,  $\sum\sigma^2 = 0.001\text{ \AA}^2$ ) with the 2 and 4 positions

(C3,4,11,12) displaced slightly toward the Ti (0.015–0.026 Å). The remaining ring carbons deviate similarly (0.002–0.028 Å) from the plane, but in the opposite direction, away from the Ti. Each pentadienyl unit is somewhat closed in contrast to complexes containing opened acyclic pd ligands.<sup>3</sup> While the internal angles are nearly 120° (119.4 (20) Å average), the C5–C6 (2.412 (10) Å) and C13–C14 (2.401 (11) Å) distances are shorter than C3–C4 (2.446 (10) Å) and C11–C12 (2.438 (11) Å), respectively.

Complex 6 can also be viewed as a monocapped trigonal prism, with the Ti atom 0.468 Å inwardly disposed from the rectangular face comprised of C5, C6, C13, and C14. The triangular faces of the monocapped tp are described by the 1-, 3-, and 5-positions of dmCh. Since these carbons are predicted to have the greatest amount of charge, the pentadienyl centroids (R1, R2) of dmCh were chosen to be the centers of the C2–C5–C6 (R1) and C10–C13–C14 (R2) triangles. The Ti–R1,R2 distances were 1.925 and 1.902 Å, respectively, and the R1–Ti–R2 angle is 155°.<sup>33</sup>

The dmCh ligands are more strongly bound to the Ti at the 2-, 3-, and 4-positions; the Ti–C2,C3,C4,C10,C11,C12 distances (2.293 (11) Å average) are ~0.1 Å shorter than the Ti–C5,C6,C13,C14 (2.391 (14) Å average) bonds to the 1- and 5-positions. A correlated lengthening of the C2–C3, C2–C4, C10–C11, and C10–C12 bonds (1.430 (10) Å average) relative to C3–C5, C4–C6, C11–C13, and C12–C14 (1.393 (4) Å average) is also observed. Steric interactions of the dimethyl units with the bound CO must play a role in causing the tilting of the dmCh ligands. Due to the dmCh slippage, the  $\pi$ -interaction resulting from  $d_{xz}$ , aided by the inward lean of ligand lobes at the 1- and 5-positions (a consequence of the envelope deformation), contributes more than that of  $d_{xy}$  to the overall  $\pi$ -bonding in the molecule.<sup>4,8</sup> Correspondingly,  $\pi$ -back-bonding from  $d_{yz}$  (a  $\delta$ -interaction) is evidenced more in the lengthening of the aforementioned C–C bonds. The syn orientation of the dmCh groups may thus be attributable to two factors: (1) the open ends of the pentadienyl units engender a sterically accessible binding site and (2) compensation for the increased repulsions in the seven-coordinate complex is provided by the predominant  $d_{xz}$   $\pi$ -bond. A minor contribution from an increased  $\sigma$ -interaction of an  $a_1$   $d_{z^2}/d_{x^2-y^2}$ -hybridized orbital upon dmCh slippage is also a possibility.

## Discussion

**Structure and Bonding.** From the variable-temperature <sup>1</sup>H NMR experiments, (dmCh)<sub>2</sub>Ti (1) possesses a gauche ground-state structure. Close examination of the IR fingerprint region of (dmCh)<sub>2</sub>V (2) reveals that its absorption bands parallel those of 1, with minor intensity and frequency shifts. Since the geometry of Ernst's ( $\eta^5$ -2,4-C<sub>7</sub>H<sub>11</sub>)<sub>2</sub>V complex is staggered ( $\chi = 89.8^\circ$ ),<sup>11</sup> it is suspected that both 1 and 2 possess similar ligand alignments. A similar pattern is also observed for (dmCh)<sub>2</sub>Cr (3), but more significant deviations in intensity are noticeable. It is thus proposed that 3 is also gauche, but perhaps less so than the Ti or V derivatives, given the  $\chi = 82.9^\circ$  value obtained for ( $\eta^5$ -2,4-C<sub>7</sub>H<sub>11</sub>)<sub>2</sub>Cr.<sup>11</sup> The IR of (dmCh)<sub>2</sub>Fe (5) exhibits distinct differences from the others, most notably the lack of a dominant band around 800 cm<sup>-1</sup>. Since variable-temperature <sup>1</sup>H NMR studies (+25 to -80 °C; C<sub>7</sub>D<sub>8</sub>) gave no indication of a gauche (C<sub>2</sub>) ground state, it is proposed that 5 possesses an anti-eclipsed, C<sub>2h</sub> geometry

in accord with calculations by Gleiter.<sup>8</sup> Analogous  $\eta^5$ -pd structures are gauche-eclipsed ( $\chi \approx 60^\circ$ ),<sup>34</sup> an orientation that is predicted to be an alternate minimum energy configuration.

There is good reason to believe that dmCh is intermediate between pd and Cp in its ability to ligate. The stable nature of the early metal derivatives is in accord with postulated strong  $\pi$ - and  $\delta$ -bonding interactions common to the related pd complexes.<sup>3,4,8</sup> Because the cyclic nature of the dmCh ligand prevents it from wrapping as efficiently about a metal, this stabilization appears somewhat lessened. Spectral evidence is consistent with this hypothesis. The  $\Delta G^\ddagger$  for dmCh oscillation in 1 (10.8 kcal/mol) is 4.5 kcal/mol less than that reported for ( $\eta^5$ -2,4-C<sub>7</sub>H<sub>11</sub>)<sub>2</sub>Ti (15.3 kcal/mol).<sup>4</sup> Substantial barriers have also been observed for ( $\eta^5$ -2,4-C<sub>7</sub>H<sub>11</sub>)<sub>2</sub>M (M = Fe,  $\Delta G^\ddagger = 9.1$  kcal/mol;<sup>34</sup> Ru, 9.7 kcal/mol),<sup>35</sup> while no hints of an analogous oscillation process for 5 have been indicated. While the latter could simply be a consequence of a different (C<sub>2h</sub>) ground-state conformation (vide supra), the data are still supportive of a smaller barrier. Curiously, while these dmCh complexes are low spin, paralleling the pd derivatives of Ernst, their colors are similar to Cp<sub>2</sub>M species, qualitatively substantiating the aforementioned ligating ability of 6,6-dimethylcyclohexadienyl.

The CO stretching frequency of (dmCh)<sub>2</sub>V–CO (7, 1912 cm<sup>-1</sup>) is intermediate between ( $\eta^5$ -2,4-C<sub>7</sub>H<sub>11</sub>)<sub>2</sub>V–CO (1942 cm<sup>-1</sup>)<sup>36</sup> and Cp<sub>2</sub>V–CO (1881 cm<sup>-1</sup>).<sup>37</sup> In each molecule, CO and ligand  $\delta$ -combinations compete for electron density from the same orbital ( $d_{yz}$  in Figure 2). From the frequencies above, CO competes with dmCh much more effectively for electron density than with 2,4-Me<sub>2</sub>-pd, but less so than in the Cp complex; therefore, the  $\delta$ -binding (M→dmCh) of 7 is probably strong, but weaker than the related pd derivative. The same arguments apply to (dmCh)<sub>2</sub>Ti–CO (6,  $\nu(\text{CO}) = 1904$  cm<sup>-1</sup>) and ( $\eta^5$ -2,4-C<sub>7</sub>H<sub>11</sub>)<sub>2</sub>Ti–CO ( $\nu(\text{CO}) = 1942$  cm<sup>-1</sup>).<sup>10</sup> Potential total disruption of  $\delta$ -bonding in (dmCh)<sub>2</sub>Ti–CO (6) upon addition of a second CO may explain why the 18-electron dicarbonyl does not form, in contrast to Cp<sub>2</sub>Ti(CO)<sub>2</sub> and the more sterically encumbered Cp\*<sub>2</sub>Ti(CO)<sub>2</sub> (Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>).<sup>38</sup>

The EPR spectra of 2, CO adduct 7, (dmCh)<sub>2</sub>V–PMe<sub>3</sub> (8), and (dmCh)<sub>2</sub>V–PF<sub>3</sub> (10) display <sup>51</sup>V hyperfine splittings significantly larger than Cp<sub>2</sub>V–CO ( $a = 27.8$  G) but comparable to their 2,4-Me<sub>2</sub>-pd congeners.<sup>11,31,36</sup> The high coupling values are attributed to population of an (assuming C<sub>2</sub> symmetry for 2) or an  $a_1$  (assuming C<sub>2v</sub> symmetry for 7, 8, and 10) orbital by the odd electron, since s–d mixing is critical. The HOMO of 2 ( $a_1^{(51\text{V})} = 54$  G) is thus thought to be a  $d_{xz^2-y^2}/d_{z^2}$  hybrid ( $z$  axis through the dmCh ligands) with some  $\delta$ -bonding character. The increase in hyperfine interaction upon addition of L (L = CO (7),  $a = 71$  G; L = PMe<sub>3</sub> (8),  $a = 76$  G; L = PF<sub>3</sub> (10),  $a = 79$  G) is attributed to an increase in the metal character of the  $a_1$  HOMO. Two  $d_{xz^2-y^2}/d_{z^2}$  hybrids exist in the adduct species ( $z$  is now taken along the V–L axis as in Figure 2). As L binds, one of these  $a_1$  orbitals becomes significantly  $\sigma^*$  with respect to CO and dmCh; the other becomes more metal-localized, effectively non-bonding.

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(33) Alternatively, using the "center of mass" of C2–6, R–Ti = 1.87 Å; C10–14, R = 1.87 Å. Using the normal to the least-squares plane of C2–6, R–Ti = 1.907 Å; C10–14, R = 1.890 Å; R–Ti–R = 152°.

The lack of significant hyperfine coupling of  $^{13}\text{C}$  in **7**- $^{13}\text{C}$  and  $^{31}\text{P}$  in **8** and **10** corroborates the contention that the latter orbital contains the odd electron.

It is not obvious why the pd derivatives, $^{31}$  especially  $(\eta^5\text{-}2,4\text{-C}_7\text{H}_{11})_2\text{V-PF}_3$  ( $a(^{31}\text{P}) = 53.6 \text{ G}$ ), $^{36}$  exhibit greater hyperfine splittings due to L. As intimated above, the electron may populate an orbital that is purely V in character, but another factor may also be influential. The pd derivatives are all stable at  $25^\circ\text{C}$  whereas  $\text{PMe}_3$  dissociates from **8** and  $\text{PF}_3$  from **10** above  $-40^\circ\text{C}$ . Since the hyperfine splitting is directly related to the amount of phosphorus character in the molecular orbital of the odd electron, the weakly bonded  $\text{PMe}_3$  and  $\text{PF}_3$  ligands of the dmCh species should provide less of a perturbation than their pd analogues. Note that  $(\text{dmCh})_2\text{V-CO}$  (**7**) is of comparable stability to  $(\eta^5\text{-}2,4\text{-C}_7\text{H}_{11})_2\text{V-CO}$  and it does manifest a hyperfine splitting ( $a(^{13}\text{C}) \approx 8 \text{ G}$ ), albeit small. Two steric factors contribute to the weaker bonding of the dmCh phosphine adducts relative to the pd species: (1) interactions of the dmCh *gem*-dimethyl envelopes with L are significant; and (2) the 1- and 5-positions of the acyclic pd ligands are further apart than the corresponding carbons in cyclic dmCh.

The essentials of the above arguments are derived from calculations of bent  $\text{Cp}_2\text{M}$  fragments conducted by Lauher and Hoffmann. $^{39}$  The HOMO is probably localized at the metal in the "wedge" between the dmCh fragments. It must also be remembered that the PES data and calculations of Gleiter, $^8$  concomitant with Mössbauer results, $^9$  draw attention to the extreme covalent nature of pd complexes and the large extent of orbital mixing, rendering any discussion of metal or ligand-localized orbitals in 1-11 subject to much interpretation.

### Experimental Section

**General Considerations.** All manipulations were performed by using either glovebox or high vacuum line techniques. Ethereal and hydrocarbon solvents were distilled under nitrogen from purple benzophenone ketyl and vacuum transferred from same prior to use. Benzene- $d_6$  and toluene- $d_8$  were dried over activated 4-Å molecular sieves, vacuum transferred, and stored under  $\text{N}_2$ . THF- $d_8$  was dried over NaK and vacuum transferred. Dimedone (5,5-dimethyl-1,3-cyclohexanedione) and 1,4-cyclohexadiene were purchased from Aldrich and used without further purification. Potassium *tert*-butoxide was sublimed ( $120^\circ\text{C}$ ,  $10^{-4}$  torr) prior to use.  $\text{TiCl}_3$ ,  $\text{TiCl}_4$  (in  $\text{CH}_2\text{Cl}_2$ , Aldrich),  $\text{CrCl}_2$ , and  $\text{FeCl}_2$  (RO-CRICH) were converted to their THF adducts $^{24}$  for purification, handling and solubility purposes.  $\text{VCl}_3$  (Cerac) and  $\text{MnCl}_2$  (Aldrich) were used without purification.

NMR spectra were recorded on Varian EM-390, XL-200, and XL-400 (variable temperature) and JEOL FX90Q (variable temperature,  $^{13}\text{C}$ ) spectrometers. Infrared spectra were obtained on a Perkin-Elmer 357 spectrometer. EPR spectra were recorded on locally modified Varian E-12 and IBM ER-200D instruments. Elemental analyses were conducted by Analytische Laboratorien, West Germany. Molecular weights were determined by benzene freezing point depression.

Measurements of the EPR and NMR spectra of the thermally labile adducts  $(\text{dmCh})_2\text{V-PMe}_3$  (**8**),  $(\text{dmCh})_2\text{V-PF}_3$  (**10**), and  $(\text{dmCh})_2\text{Ti-PF}_3$  (**9**) were conducted in sealed tubes. For example, 10 mg of  $(\text{dmCh})_2\text{Ti}$  (**1**, 0.038 mmol) was placed in an NMR tube sealed to a ground glass joint fitted to a needle valve adapter. The tube was evacuated and cooled to 77 K.  $\text{C}_7\text{D}_8$  (0.4 mL) was distilled in,  $\text{PF}_3$  (0.040 mmol) admitted via a gas bulb, and the tube sealed with a torch.

**Procedures.** 1. **5,5-Dimethyl-1,3-cyclohexadiene, (dmCh)H.** To a slurry of dimedone (50.0 g, 0.357 mol) in 300 mL of  $\text{Et}_2\text{O}$  cooled to  $0^\circ\text{C}$  was slowly added  $\text{LiAlH}_4$  (12.8 g, 0.337 mol). The resulting slurry was allowed to warm to  $25^\circ\text{C}$  and

stirred for 2 h. Another portion of  $\text{LiAlH}_4$  (7.7 g, 0.20 mol) was then added, and the mixture was gently heated to reflux for 2 h. The reaction was then sequentially quenched with  $\text{H}_2\text{O}$  (20 mL), 20 mL of 15% aqueous NaOH, and 60 mL of  $\text{H}_2\text{O}$ . After filtration, the ether layer was washed with  $\text{H}_2\text{O}$  and dried over  $\text{MgSO}_4$  to give crude 5,5-dimethyl-1,3-cyclohexanediol ( $\sim 33.7 \text{ g}$ , 65%). The crude diol was treated with 9 M  $\text{H}_2\text{SO}_4$  (10 mL, 0.09 mol) and vigorously stirred while slowly heated to  $130^\circ\text{C}$  for 1.5 h. Fractions boiling less than  $97^\circ\text{C}$  were collected, combined, diluted with  $\text{Et}_2\text{O}$  (50 mL), washed with 10%  $\text{Na}_2\text{CO}_3$  and water, and dried over  $\text{MgSO}_4$ . Rotovapping, distillation at  $45^\circ\text{C}$ , and final distillation ( $25^\circ\text{C}$ ,  $10^{-4}$  torr) afforded  $(\text{dmCh})\text{H}$  (18.5 g, 74% from diol, 45% overall) diluted with variable portions of  $\text{Et}_2\text{O}$  but sufficiently pure for further use.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.96 (s,  $\text{CH}_3$ , 6 H), 2.07 (dd,  $\text{CH}_2$ , 2 H,  $^3J = 4 \text{ Hz}$ ,  $^4J = 2 \text{ Hz}$ ), 5.6 (m,  $-\text{CH}=\text{}$ , 4 H).

2. **6,6-Dimethylcyclohexadienylpotassium, (dmCh)K.** To a solution of KO-*t*-Bu (14.7 g, 0.131 mol) in 100 mL of THF was added  $(\text{dmCh})\text{H}$  (14.2 g, 0.131 mol) diluted with  $\text{Et}_2\text{O}$  (used directly as in 1.). The solution was cooled to  $-78^\circ\text{C}$ , and *n*-BuLi (85.0 mL, 0.132 mol, 1.55 in hexane) was added via syringe. After 5 min, a yellow precipitate was observed. Stirring continued for 3 h, and the slurry was warmed to  $25^\circ\text{C}$  and evaporated to dryness. The yellow residue was ground to a powder and washed with 50-mL portions of  $\text{Et}_2\text{O}$  until the washings were colorless. Filtration from an  $\text{Et}_2\text{O}$  slurry provided 17.2 g (90%) of pyrophoric yellow powder. $^{23}$   $^1\text{H NMR}$  (THF- $d_8$ ):  $\delta$  0.71 (s,  $\text{CH}_3$ , 6 H), 3.34 (dd,  $\text{H}_c$ , 2 H,  $^3J = 7 \text{ Hz}$ ,  $^4J < 1 \text{ Hz}$ ), 3.69 (tt,  $\text{H}_a$ , 1 H,  $^3J = 6 \text{ Hz}$ ,  $^4J = < 1 \text{ Hz}$ ), 5.75 (dd,  $\text{H}_b$ , 2 H,  $^3J = 7 \text{ Hz}$ ,  $^4J = 6 \text{ Hz}$ ).

3. **General Procedure:  $(\eta^5\text{-}6,6\text{-Me}_2\text{-C}_6\text{H}_5)_2\text{M}$ ,  $(\text{dmCh})_2\text{M}$ .** To a slurry of  $\text{MX}_n$  in THF at  $-78^\circ\text{C}$  was added *n* equiv of  $(\text{dmCh})\text{K}$  from a solid addition funnel over a 3-h period. Alternatively, a THF solution of  $\text{K}(\text{dmCh})$  was added via a dropping funnel over the same period. The reaction mixture was stirred for 4 h, allowed to warm to  $25^\circ\text{C}$ , and stirred for an additional 12 h. The THF was removed, pentane was added, and the solution filtered. Removal of pentane afforded  $(\text{dmCh})_2\text{M}$  and  $\text{C}_{16}\text{H}_{22}$ .

a.  **$(\text{dmCh})_2\text{Ti}$  (**1**).** From  $\text{TiCl}_3(\text{THF})_3$  (508 mg, 1.37 mmol) or  $\text{TiCl}_4(\text{THF})_2$  and  $(\text{dmCh})\text{K}$  (601 mg, 4.11 mmol) in 50 mL of THF, crude **1** ( $\sim 180 \text{ mg}$ , 50%) was obtained.

b.  **$(\text{dmCh})_2\text{V}$  (**2**).** From  $\text{VCl}_3$  (286 mg, 1.82 mmol) and  $(\text{dmCh})\text{K}$  (0.800 g, 5.47 mmol) in 50 mL of THF, crude **2** ( $\sim 202 \text{ mg}$ , 42%) was obtained.

c.  **$(\text{dmCh})_2\text{Cr}$  (**3**).** From  $\text{CrCl}_2(\text{THF})_2$  (457 mg, 1.71 mmol) and  $(\text{dmCh})\text{K}$  (500 mg, 3.42 mmol) in 45 mL of THF, crude **3** was obtained. Sublimation of the residue ( $40^\circ\text{C}$ ,  $10^{-4}$  torr) afforded 308 mg (68%) of crimson, crystalline **3**. Anal. Calcd for  $\text{C}_{16}\text{H}_{22}\text{Cr}$ : C, 72.15; H, 8.33. Found: C, 71.98; H, 8.41. IR ( $\text{C}_6\text{H}_{12}$ ,  $\text{cm}^{-1}$ ): 3050 w, 2950 w, 1389 w, 1369 s, 1354 s, 1295 w, 1222 w, 1163 s, 1119 s, 1052 m, 988 m, 964 w, 940 m, 817 s, 783 w, 756 m, 733 m, 720 w, 621 m, 525 w, 564 m.

d.  **$(\text{dmCh})_2\text{Mn}$  (**4**).** From  $\text{MnCl}_2$  (215 mg, 1.71 mol) and  $(\text{dmCh})\text{K}$  (500 mg, 3.42 mmol) in 30 mL of THF, crude **4** was obtained as a deep pink oil contaminated with  $\text{C}_{16}\text{H}_{22}$ . The estimated crude yield is low ( $\sim 15\%$ ), and a substantial amount of Mn metal precipitates. When crude **4** is treated with  $\text{FeCl}_2$ , the pink solution slowly became orange and  $^1\text{H NMR}$  indicated the presence of  $(\text{dmCh})_2\text{Fe}$  (**5**).

e.  **$(\text{dmCh})_2\text{Fe}$  (**5**).** From  $\text{FeCl}_2(\text{THF})_2$  (470 mg, 1.71 mmol) and  $(\text{dmCh})\text{K}$  (500 mg, 3.42 mmol) in 35 mL of THF, crude **5** was obtained. Crystallization from pentane provided 195 mg of red-orange **5** (42%). Anal. Calcd for  $\text{C}_{16}\text{H}_{22}\text{Fe}$ : C, 71.12; H, 8.21. Found: C, 71.18; H, 8.15. IR ( $\text{C}_6\text{H}_{12}$ ,  $\text{cm}^{-1}$ ): 3030 w, 3005 w, 1375 s, 1358 s, 1305 m, 1177 s, 1119 w, 1057 m, 1002 m, 964 w, 949 m, 922 w, 849 m, 828 m, 793 m, 782 w, 621 m, 611 w, 532 m, 518 m, 473 m, 442 m.

4.  **$(\text{dmCh})_2\text{Ti-CO}$  (**6**).** In 25 mL of hexane, crude **1** ( $\sim 180 \text{ mg}$ , 0.68 mmol) was exposed to 1 atm of CO at  $25^\circ\text{C}$ . The dark green solution immediately turned cherry red. Crystallization from hexane afforded needles of red-orange **6** in 95% yield (188 mg). In the solid state, **6** was thermally sensitive, decomposing to an amorphous black solid of unknown composition. IR (Nujol):  $\nu(\text{CO})$  1904  $\text{cm}^{-1}$ . IR (cyclohexane,  $\text{cm}^{-1}$ ): 3060 w, 3000 w, 1904 (CO) vs, 1381 s, 1360 s, 1295 m, 1192 w, 1155 m, 1115 m, 1050 s, 985 m, 935 m, 820 w, 805 s, 748 m, 634 m, 529 m, 510 w, 490 m, 470 m.

(39) (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729-1742. (b) Hoffmann, R.; Hofmann, P. *Ibid.* **1976**, *98*, 598-604.



5.  $(dmCh)_2V-CO$  (7). In 25 mL of hexane, crude 2 (~220 mg, 0.83 mmol) was exposed to 1 atm of CO at 25 °C. The solution turned from scarlet to brown over the course of 20 min. Crystallization from hexane gave 219 mg of yellow-green needles of 7 (90%). Anal. Calcd for  $C_{17}H_{22}OV$ : C, 69.65; H, 7.56. Found: C, 69.34; H, 7.47. IR (Nujol):  $\nu(CO)$  1917  $cm^{-1}$ . IR (cyclohexane,  $cm^{-1}$ ): 3050 w, 2990 w, 1912 (CO) vs, 1381 s, 1350 m, 1300 w, 1210 w, 1161 m, 1119 m, 1060 m, 991 m, 970 m, 946 m, 910 wbr, 830 s, 813 m, 765 m, 730 w, 685 w, 635 w, 550 m, 508 s, 490 w, 470 w.

6. Purification of  $(dmCh)_2Ti$  (1). A sample of recrystallized 6 (167 mg, 0.58 mmol) was dissolved in 10 mL of toluene and transferred to a 200-mL glass bomb reactor containing a needle valve adapter. The solution was degassed, and the vessel was immersed in an 80 °C bath for 24 h. At frequent intervals (~6), the reactor was degassed while hot. After cooling and removal of solvent, forest-green crystalline solid remained. Sublimation (25 °C,  $10^{-4}$  torr) afforded 1 in 76% yield (119 mg, 38% based on  $TiCl_3$ ). Anal. Calcd for  $C_{16}H_{22}Ti$ : C, 73.28; H, 8.46;  $M_r$ , 262. Found: C, 73.06; H, 8.32;  $M_r$ , 215. IR ( $C_6H_{12}$ ,  $cm^{-1}$ ): 3040 w, 3010 w, 1363 s, 1355 m, 1282 w, 1247 w, 1197 w, 1180 w, 1152 m, 1114 s, 1046 m, 976 m, 935 w, 902 w, 877 wbr, 788 vs, 740 w, 721 w, 710 w, 679 m, 618 m, 519 m, 457 m.

7. Purification of  $(dmCh)_2V$  (2). Crude 2 (~252 mg, 0.950 mmol) was dissolved in 10 mL of hexane and cooled to -78 °C. An excess of  $PMe_3$  (1 mL, 10 mmol) was condensed in via a glass bulb. An immediate brown precipitate was evidenced. Via syringe, 10 mL of pentane was added and the precipitate allowed to settle. Approximately 8 mL of the supernatant was extracted and discarded. The extraction was repeated twice, and the solvent and released  $PMe_3$  were removed in vacuo affording scarlet crystals of 2. Sublimation (25 °C,  $10^{-4}$  torr) provided 210 mg (35%, based on  $VCl_3$ ). Anal. Calcd for  $C_{16}H_{22}V$ : C, 72.44; H, 8.36. Found: C, 72.33; H, 8.22. IR ( $C_6H_{12}$ ,  $cm^{-1}$ ): 3050 w, 3015 w, 1391 w, 1371 s, 1360 m, 1208 w, 1200 wbr, 1185 w, 1150 m, 1119 s, 1051 m, 982 m, 960 m, 935 w, 910 wbr, 812 vs, 769 w, 752 m, 720 m, 710 w, 621 m, 528 m, 460 m.

8.  $(\eta^5-C_6H_7)_2Fe, CH_2Fe$  (11). To 30 mL of THF and LDA (1.34 g, 12.5 mmol) at -78 °C was added 1.20 mL (1.00 g, 12.5 mmol) of 1,4-cyclohexadiene. At -78 °C, the color deepened from lemon yellow to deep yellow-orange over a 1.5-h period. Still at -78 °C,  $FeCl_2$  (790 mg, 6.24 mmol) was added via side arm over 2 h. The mixture was stirred for 8 h and the resulting brown solution allowed to warm to 25 °C. The THF was removed, hexane added, and the red-orange solution filtered. Crystallization from hexane gave 610 mg of 11 (46%).  $CH_2Fe$  is thermally unstable in the solid state (25 °C), isomerizing to  $(\eta^6-C_6H_8)Fe(\eta^4-1,3-C_6H_8)$  (12).<sup>32</sup>  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  1.92 (d,  $H_{exo}$ , 2 H,  $^2J = 13$  Hz), 2.59 (dd,  $H_{c,c'}$ , 4 H,  $^3J = 7$ ,  $^3J = 6$  Hz), 2.67 (dt,  $H_{endo}$ , 2 H,  $^2J = 13$ ,  $^3J = 7$  Hz), 4.04 (dd,  $H_{b,b'}$ , 4 H,  $^3J = 7$ ,  $^3J = 6$  Hz), 4.76 ("t",  $H_a$ , 2 H,  $^3J = 7$  Hz).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  26.98 ( $CH_2$ ), 35.03 ( $CH_c, CH_c'$ ), 77.86 ( $CH_a$ ), 86.51 ( $CH_b, CH_b'$ ).

9.  $(dmCh)_2, C_{16}H_{22}, 3-(4,4-Dimethyl-2,5-cyclohexadien-1-yl)-6,6-dimethyl-1,4-cyclohexadiene$ . To a solution of  $ZnCl_2$  (139 mg, 1.03 mmol) in 25 mL of THF at -78 °C was added solid  $(dmCh)K$  (300 mg, 2.06 mmol). Over a 20-min period, the red color of the anion was slowly discharged to give a colorless solution. When the solution was warmed to 25 °C, the formation of Zn metal was noted. The THF was removed, hexane was added, the solution was filtered, and the volatiles were evaporated to give 132 mg (60%) of a colorless oil.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.02 (s,  $CH_3$ , 12 H),  $\delta$  2.83 (br s, CH, 2 H), 5.53 (m, =CH-, 8 H).  $^{13}C$  NMR  $\delta$  136.3 (=CH-), 124.2 (=CH-), 40.2 ( $C(CH_3)_2$ ), 33.2 (CH), 30.5 ( $CH_3$ ), 30.4 ( $CH_3$ ).

Single-Crystal X-ray Diffraction Analysis of  $(dmCh)_2Ti-CO$  (6). A truncated needle (approximately  $0.6 \times 0.3 \times 0.2$  mm) of  $(dmCh)_2Ti-CO$  (6), obtained via sublimation (25 °C,  $10^{-4}$  torr), was sealed in a Lindemann capillary. Preliminary X-ray diffraction photographs displayed monoclinic symmetry. Precise lattice constants, determined from a least-squares fit of 15 diffractometer measured  $2\theta$  values at 25 °C, were  $a = 7.372$  (1) Å,  $b = 9.900$  (1) Å,  $c = 22.101$  (3) Å, and  $\beta = 105.100$  (8)°. The cell volume was  $1557.3$  Å<sup>3</sup> with a calculated density of  $1.238$  g/cm<sup>3</sup> where  $Z = 4$ . The space group was uniquely determined to be  $P2_1/n$  and the asymmetric unit consisted of  $C_{17}H_{22}OTi$ . All unique diffraction maxima ( $h,k,\pm l$ ) with  $2\theta \leq 107^\circ$

Table III. Fractional Coordinates and Thermal Parameters<sup>a</sup> for  $(dmCh)_2Ti-CO$  (6)

atom	x	y	z	B(iso), Å <sup>2</sup>
Ti	0.4143 (2)	0.0354 (1)	0.1345 (1)	5.4 (0)
C1	0.1390 (11)	0.0088 (7)	0.1089 (3)	6.7 (3)
O1	-0.0237 (7)	-0.0064 (6)	0.0949 (3)	8.8 (2)
C2	0.6758 (9)	-0.0816 (7)	0.1883 (3)	5.8 (2)
C3	0.5927 (9)	-0.1543 (7)	0.1322 (3)	5.6 (2)
C4	0.5618 (10)	-0.0526 (7)	0.2299 (3)	6.0 (2)
C5	0.4112 (9)	-0.2040 (7)	0.1219 (3)	5.6 (2)
C6	0.3806 (10)	-0.1057 (7)	0.2186 (3)	6.0 (2)
C7	0.3417 (10)	-0.2365 (7)	0.1805 (3)	5.8 (2)
C8	0.1349 (11)	-0.2819 (8)	0.1662 (4)	7.8 (3)
C9	0.4640 (11)	-0.3527 (8)	0.2187 (4)	7.2 (3)
C10	0.6278 (10)	0.1985 (7)	0.1252 (3)	6.6 (3)
C11	0.5379 (10)	0.1479 (8)	0.0634 (3)	6.5 (3)
C12	0.5078 (12)	0.2523 (7)	0.1602 (3)	7.0 (3)
C13	0.3442 (10)	0.1630 (7)	0.0401 (3)	5.9 (2)
C14	0.3151 (11)	0.2671 (7)	0.1353 (3)	6.6 (3)
C15	0.2490 (11)	0.2842 (7)	0.0633 (3)	6.6 (3)
C16	0.0346 (11)	0.2844 (9)	0.0383 (4)	8.4 (3)
C17	0.3292 (12)	0.4168 (8)	0.0432 (4)	8.2 (3)
H2	0.8147	-0.0517	0.1986	6.6
H3	0.6670	-0.1703	0.0990	6.5
H4	0.6130	0.0093	0.2685	7.0
H5	0.3262	-0.2189	0.0766	6.7
H6	0.2759	-0.0572	0.2343	7.0
H8	0.0963	-0.3001	0.2067	8.8
H8'	0.0477	-0.2099	0.1408	8.8
H8''	0.1155	-0.3703	0.1401	8.8
H9	0.4475	-0.4411	0.1933	8.1
H9'	0.6041	-0.3267	0.2295	8.1
H9''	0.4283	-0.3709	0.2598	8.1
H10	0.7734	0.1967	0.1430	7.5
H11	0.6175	0.0993	0.0378	7.6
H12	0.5645	0.2809	0.2065	7.6
H13	0.2622	0.0942	0.0080	7.0
H14	0.2167	0.2648	0.1629	7.5
H16	-0.0063	0.2874	-0.0096	9.3
H16'	-0.0222	0.1954	0.0519	9.3
H16''	-0.0261	0.3633	0.0556	9.3
H17	0.2775	0.4999	0.0602	8.6
H17'	0.4745	0.4182	0.0596	8.6
H17''	0.2973	0.4239	-0.0050	8.6

<sup>a</sup> From the anisotropic thermal parameters in the form  $exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ , the  $B$ (iso) (thermal equivalents) are derived:  $B(iso) = 4.0[V^2\det(\beta_{ij})]^{1/3}$ .

were measured on a four-circle, computer-controlled diffractometer with a variable  $1^\circ \omega$  scan ( $0.1-30^\circ/\text{min}$ ) using graphite-monochromated  $Cu K\alpha$  radiation ( $\lambda = 1.54178$  Å) at 25 °C. After correction for Lorentz polarization and background effects, 1356 (79%) of the 1721 reflections collected were judged observed ( $|F_o| \geq 3\sigma(F_o)$ ).<sup>40</sup> Structure solution using heavy-atom techniques proceeded routinely.<sup>41</sup> The Ti was positioned from the Patterson synthesis, and the non-hydrogen light atoms revealed by successive Fourier syntheses. Block-diagonal least-squares refinements (minimization of  $\sum w(|F_o| - |F_c|)^2$ , where  $w$  is based on counting statistics modified by an ignorance factor of  $\rho = 0.03$ ) with 19 anisotropic non-hydrogen atoms and all hydrogen atoms included at calculated positions have converged to a residual ( $R$ ) of 0.074 and a weighted residual ( $R_w$ ) of 0.076 (173 parameters, reflec-

(40) All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were as follows: REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN 78, a system of computer programs for the automatic solutions of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978; BLS78A, an anisotropic block-diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, an illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu, Cornell University, 1978.

(41) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A*: 1968, A24, 321.

tions/parameter = 7.8).<sup>42</sup> The fractional coordinates and thermal parameters are listed in Table III.

**Acknowledgment.** Support from the Cornell National Research and Resource Facility for Submicron Structures (NRRFSS) and partial support from the National Science Foundation (CHE-8308272), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Cornell University is gratefully acknowledged. We thank the Exxon Educational Foundation for a fellowship (P.T.D.), Prof. Jon C. Clardy, Gregory D. Van Duyne, and the Chem 789 class for X-ray structural work, and the NIH and NSF Instrumentation Programs for

support of the Cornell NMR and EPR Facilities.

**Registry No.** 1, 108969-10-4; 2, 108969-11-5; 3, 108969-12-6; 4, 108969-13-7; 5, 108969-14-8; 6, 109011-04-3; 7, 108969-15-9; 8, 108969-16-0; 9, 108969-17-1; 10, 108969-18-2; 11, 108969-19-3; 12, 71265-76-4; (dmCh)H, 33482-80-3; (dmCh)K, 82360-21-2; (dmCh)<sub>2</sub>, 108947-34-8; TiCl<sub>3</sub>(THF)<sub>3</sub>, 18039-90-2; TiCl<sub>4</sub>(THF)<sub>2</sub>, 31011-57-1; CrCl<sub>2</sub>(THF)<sub>2</sub>, 15604-50-9; FeCl<sub>2</sub>(THF)<sub>2</sub>, 70317-90-7; VCl<sub>3</sub>, 7718-98-1; MnCl<sub>2</sub>, 7773-01-5; FeCl<sub>2</sub>, 7758-94-3; 5,5-dimethyl-1,3-cyclohexanedione, 126-81-8; 5,5-dimethyl-1,3-cyclohexanediol, 597-98-8; 1,4-cyclohexadiene, 628-41-1.

**Supplementary Material Available:** Tables of bond distances, bond angles, fractional coordinates, thermal parameters, and least-squares planes calculations (11 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

$$(42) R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; R_w = \frac{\{\sum w|F_o| - |F_c|\}^2}{(\sum w|F_o|)^2}^{1/2}.$$

## Crystallographic and Theoretical Analyses of the Structures of Rhenium Formyl and Acyl Complexes of the Formula $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PR}_3)(\text{COR}')$

Gerardo S. Bodner,<sup>1a</sup> Alan T. Patton,<sup>1a</sup> Danny E. Smith,<sup>1a</sup> Savas Georgiou,<sup>1a</sup> Wilson Tam,<sup>1b</sup> Wai-Kwok Wong,<sup>1b</sup> Charles E. Strouse,<sup>1b</sup> and J. A. Gladysz\*<sup>1,2</sup>

Departments of Chemistry, University of Utah, Salt Lake City, Utah 84112, and University of California, Los Angeles, California 90024

Received January 29, 1987

X-ray crystal structures of formyl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CHO})$  (1) and acyl complex  $(SR\text{-}RS)\text{-}(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{COCH}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5)\cdot(\text{THF})_{0.5}$  (2 $\cdot$ (THF)<sub>0.5</sub>) are reported. Crystal data: 1, monoclinic,  $P2_1/c$ ,  $a = 8.065$  (3) Å,  $b = 15.156$  (3) Å,  $c = 16.896$  (4) Å,  $\beta = 95.44$  (2)°,  $Z = 4$ ; 2 $\cdot$ (THF)<sub>0.5</sub>, triclinic,  $P\bar{1}$ ,  $a = 17.844$  (4) Å,  $b = 11.101$  (2) Å,  $c = 9.704$  (2) Å,  $\alpha = 64.62$  (2)°,  $\beta = 75.55$  (2)°,  $\gamma = 73.20$  (2)°,  $Z = 2$ . Extended Hückel MO calculations on model compounds  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PH}_3)(\text{COR})$  predict that the ON-Re-C $\alpha$ -O torsion angle ( $\theta$ ) should be near 0° or 180°, so that overlap of the rhenium fragment HOMO with the C=O  $\pi^*$  orbital will be maximized. Accordingly, Re-C $\alpha$  conformations with  $\theta$  near 180° are found in 1 and 2 $\cdot$ (THF)<sub>0.5</sub>. This places the C=O oxygen anti to the NO ligand. The geometries of the formyl and acyl ligands are contrasted and compared to those of other formyl and acyl complexes.

### Introduction

While metal formyl complexes ( $L_n\text{MCHO}$ ) and acyl complexes ( $L_n\text{MCOR}$ ) have many physical similarities, they exhibit strikingly different chemical properties.<sup>3</sup> The former are good hydride ( $\text{H}^-$ )<sup>3-5</sup> and hydrogen atom ( $\text{H}\cdot$ )<sup>6</sup> donors, whereas the latter are not ready sources of carbanions ( $\text{R}^-$ ) or alkyl radicals ( $\text{R}\cdot$ ). Formyl complexes are generally thermodynamically unstable with respect to hydride complexes ( $L_n\text{MH}$ ) and carbon monoxide,<sup>3,7,8</sup>

whereas most acyl complexes are stable with respect to alkyl complexes ( $L_n\text{MR}$ ) and carbon monoxide.<sup>7a,d,9</sup> These contrasting properties are of interest in that both types of complexes play an important role in catalytic CO/H<sub>2</sub> chemistry. For example, formyl complexes are highly probable intermediates in the homogeneously catalyzed conversion of CO/H<sub>2</sub> to oxygenates.<sup>10</sup> Acyl complexes are

- (1) (a) University of Utah. (b) UCLA.  
 (2) Address correspondence to this author at the University of Utah.  
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