and the complex $Fe_2(\mu\text{-}t\text{-}Bu_2P)_2Cl_2(PMe_3)_2$ (**1**) appears to our knowledge to be only the second d^6 "tetrahedral dimer" of the iron triad to have been structurally characterized. (ii) The stabilization of a mixed-valence complex: here the cobalt compound $Co_2(\mu\text{-}t\text{-}Bu_2P)_2Cl(PMe_3)_2$ (**2**) has a relatively rare Co(II)–Co(I) formal oxidation state due to the presence of one terminal chloride ligand on one cobalt. (iii) Coordinative unsaturation: all three complexes are coordinatively unsaturated and none obeys the 18-electron rule. The Ni(I) dimer $[Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (**3**) is a key member of a class of unsaturated dinuclear phosphido-bridged complexes of Ni(I). Stable complexes of Ni(I) are rare, and so far only one other member of this class has been structurally characterized. (iv) Last, a key structural feature in each case is the presence of the dinuclear $M_2(\mu\text{-}t\text{-}Bu_2P)_2$ core in which the M_2P_2 unit is planar and the internuclear distances suggest the presence of metal–metal bonding. Since a number of bis(phosphido)-bridged dimers have a "butterfly" arrangement of the $\mu\text{-}PR_2^-$ units and a "bent" metal–metal bond,[11] we have investigated the possibility that the planarity might be due mainly to electronic factors. However, preliminary results appear to discount this.[12] Instead studies using space-filling CPK models suggest that the planarity is due to steric reasons. The two *t*-Bu groups on each phosphido phosphorus atom occupy considerable space and permit relatively small non-bonded H···H contacts between neighboring *t*-Bu methyl groups. Similar modeling studies of $M_2(\mu\text{-}Ph_2P)_2$ and $M_2(\mu\text{-}Me_2P)_2$ cores clearly show that steric effects are relatively unimportant in determining their framework geometries.

The use of excess $Li\text{-}t\text{-}Bu_2P$ in the synthesis of the iron complex $Fe_2(\mu\text{-}t\text{-}Bu_2P)_2Cl_2(PMe_3)_2$ (**1**) results in considerable decomposition, and we have been unable to isolate any pure products under these conditions. Also, **1** is unstable in hydrocarbon solutions, rapidly producing paramagnetic decomposition products, and it can be isolated in only very low yield. This has so far precluded its full spectroscopic characterization.

The solid-state structure, however, is of considerable interest (Figure 1). The terminal PMe_3 and Cl ligands give each d^6 iron(II) atom a roughly tetrahedral geometry (excluding the Fe-Fe bond, ca. 2.8 Å, in the geometry of each Fe atom). Very few mononuclear Fe(II) complexes such as $FeCl_4^{2-}$ and FeL_4^{2+} (L = Ph_3PO, $(Me_2N)_3PO$) are known.[10] Although the "tetrahedral" d^6 dimer $Ru_2Cl_6^{2+}$[13] has been structurally characterized, this geometry is more common for d^8 complexes such as $[Ru(NO)(\mu\text{-}PPh_2)(PPh_3)]_2$[14] and $[Ir(CO)(\mu\text{-}PPh_2)(PPh_3)]_2$.[15] The Fe–Fe distance (ca. 2.8 Å) represents a weak interaction since it is significantly longer than the single bond lengths required by the $Fe_2(CO)_6(PR_2)_2$ dimers to satisfy the 18-electron rule.[16]

By virtue of its asymmetric structure in which there is one terminal chloride ligand, the cobalt(II,I) complex $Co_2(\mu\text{-}t\text{-}Bu_2P)_2Cl(PMe_3)_2$ is a particularly interesting example of a dinuclear formally mixed-valence species containing a metal–metal interaction.[17] The geometry of the tetrahedral, formally Co(II), end is very similar to one end of the Fe(II) dimer (**1**). The PMe_3 group on the other cobalt(I) atom lies in the $Co_2(\mu\text{-}t\text{-}Bu_2P)_2$ plane so that it is nearly colinear (Co(2)–Co(1)–P(3) = 168.3 (1)°) with the metal–metal bond. As expected (**2**) is paramagnetic (μ_{eff} = 1.70 μB per dimer, by Evans' method in solution), indicating one unpaired electron per molecule. However, we have not observed an EPR signal in benzene solution at room temperature or at −196 °C.

As noted above $[Ni(\mu\text{-}t\text{-}Bu_2P)PMe_3]_2$ (**3**) is a member of a relatively rare class of nickel(I) phosphido bridged compounds for which structural data is available on only one.[18] For **3** $^{31}P\{^1H\}$ NMR data[18] are in accord with the X-ray crystal structure in which all the phosphorus and nickel atoms are coplanar and the $Me_3P\text{–}Ni\text{–}Ni\text{–}PMe_3$ unit is linear, giving the molecule D_{2h} symmetry. The Ni–Ni separation of 2.375 (3) Å is in accord with a single metal–metal bond, giving each nickel atom an unsaturated 16-electron configuration.

Further studies on the chemistry of these complexes and of bulky phosphido complexes in general are in progress.

Acknowledgment. We thank the Dow Chemical Company, Midland, MI, and the Robert A. Welch Foundation (R.A.J.) and the National Science Foundation (J.L.A.) for financial support.

Registry No. $\{Fe(\mu\text{-}t\text{-}Bu_2P)Cl(PMe_3)\}_2$, 82808-28-4; $Co_2(\mu\text{-}t\text{-}Bu_2P)_2Cl(PMe_3)_2$, 82918-17-0; $\{Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)\}_2$, 82808-29-5; $FeCl_2(PMe_3)_2$, 55853-16-2; $CoCl_2(PMe_3)_2$, 53432-22-7; $NiCl_2(PMe_3)_2$, 19232-05-4; $Li\text{-}t\text{-}Bu_2P$, 19966-86-0; Fe, 7439-89-6; Co, 7440-48-4; Ni, 7440-02-0.

Supplementary Material Available: Tables of final fractional coordinates, bond distances and angles, anisotropic thermal parameters, and structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

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Carbon Monoxide Activation by Organoactinides. Formyl Pathways in CO Homologation and Hydrogenation[†]

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Received August 12, 1982

Summary: The carbonylation of $Th[(CH_3)_5C_5]_2(OR)H$ (R = $CH[C(CH_3)_3]_2$) to yield an enediolate, $\{Th[(CH_3)_5C_5]_2OR\}_2[cis\text{-}OC(H){=}C(H)O\text{-}]$, or, in the presence of H_2, the methoxide $Th[(CH_3)_5C_5]_2(OR)(OCH_3)$ is argued on the basis of chemical and kinetic evidence to involve rate-limiting attack of a carbene-like η^2-formyl ($Th(\eta^2\text{-}OCH)$) on a Th–H functionality to produce a $ThOCH_2Th$

[†] This contribution is dedicated to Professor Rowland Pettit, whose work continues to inspire us all.

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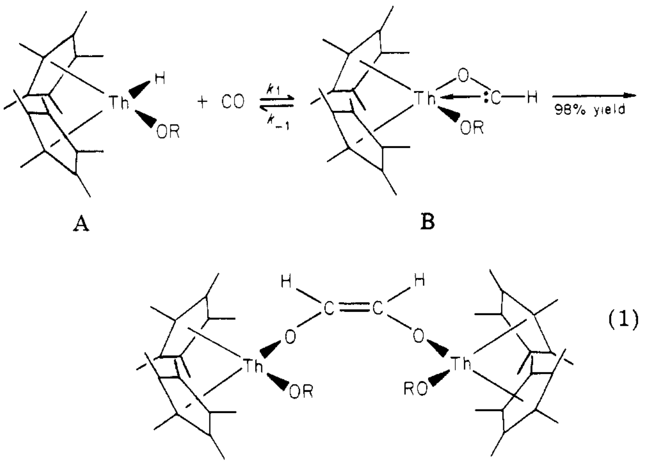
intermediate. The intermediate suffers subsequent carbonylation and rearrangement to yield the enediolate or hydrogenolysis to yield the methoxide.

We recently reported the rapid, reversible migratory insertion of CO into thorium–hydrogen bonds (A) to yield mononuclear η^2-formyls (B, eq 1), followed by a slower (the rate a sensitive function of R) coupling reaction to yield *cis*-enediolates (C).[1] The unusual character of this efficient, regiospecific carbon–carbon double bond-forming process, apparent analogues of which also exist for other actinide[2] as well as early transition-metal[3] and main-group[4] compounds, has prompted a mechanistic investigation. We communicate here evidence that for R = $CH[C(CH_3)_3]_2$ the rate-limiting step in this transformation involves metal hydride attack on the η^2-formyl and that the course of the reaction can be easily diverted to effect clean CO hydrogenation to a methoxide.

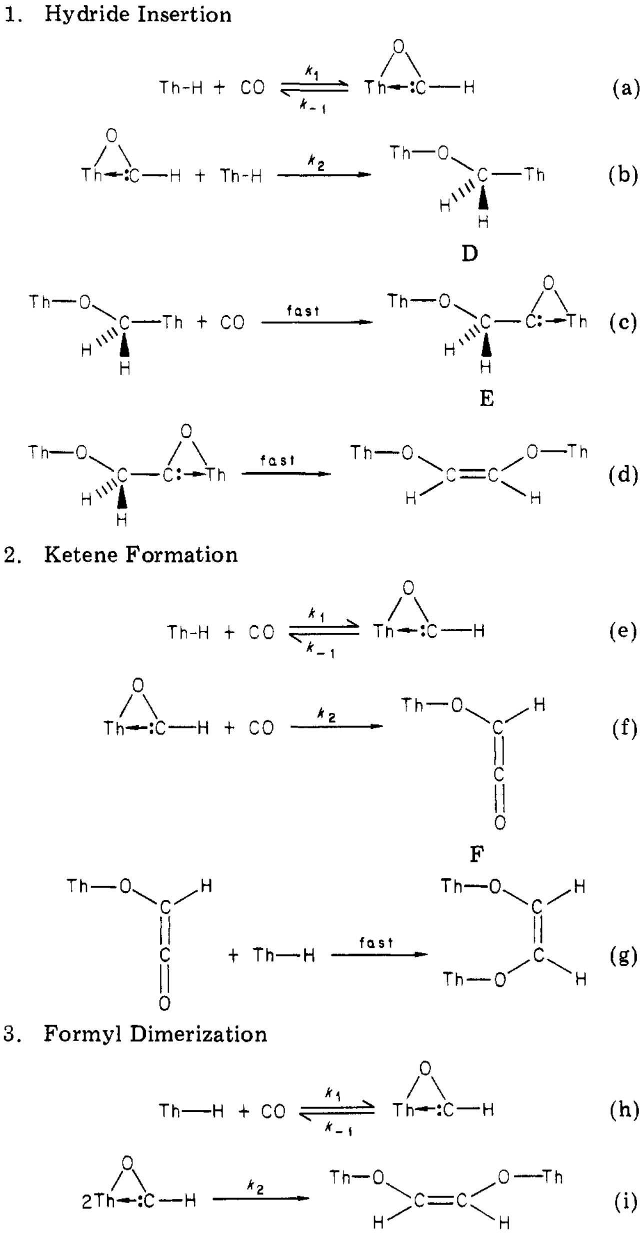


C

(1)

A priori, three mechanistic sequences seem most reasonable for enediolate formation (Scheme I) and can be tested against kinetic/chemical information. A hydride insertion reaction (scenario 1) finds precedent in d- and f-element η^2-acyl chemistry[2a,5,6] and, with use of the previously obtained kinetic and thermodynamic data for step a,[1,7] the sequence can be analyzed by standard, steady-state approximation methods.[8,9a] Thus, as written, scenario 1 predicts rate ∝ $[Th]^2[CO]$. There is ample precedent in organoactinide chemistry for the postulated rapidity of step c relative to k_2 (especially for bulky hydrocarbyl groups)[2,3,10,11] and for the carbene-like hydrogen atom

Scheme I



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(7) We estimate that $k_{-1} \gtrsim 10^4\ s^{-1}$ from NMR line shapes[1] and from thermodynamic measurements[1] that $K = k_1/k_{-1} = 3.2\ (5)\ M^{-1}$ at 30 °C. It will be seen that $k_2 \approx 0.3\ M^{-1}\ s^{-1}$.

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(9) The steady-state and equilibrium assumptions reduce to the same expressions.

(a) $$\frac{d[ThH]}{dt} = -\frac{k_1k_2[ThH]^2[CO]}{k_{-1} + k_2[ThH]} \approx -\frac{k_1k_2}{k_{-1}}[ThH]^2[CO]$$

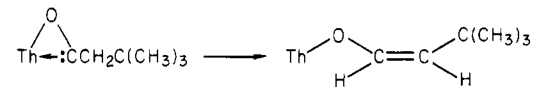
where $k_2[ThH]/k_{-1} < 10^{-5}$ under the present conditions ([ThH] ≈ 0.05 M, $P_{CO} \lesssim 760$ torr).[7]

(b) $$\frac{d[ThH]}{dt} = -\frac{k_1k_2[ThH][CO]^2}{k_{-1} + k_2[CO]} \approx -\frac{k_1k_2}{k_{-1}}[ThH][CO]^2$$

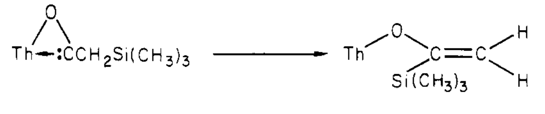
where $k_2[CO] \ll k_{-1}$ under the present conditions.[7,18]

(c) $$\frac{d[ThH]}{dt} = -k_2\left[\frac{k_1[ThH][CO]}{k_{-1} + k_2[ThCHO]}\right]^2 \approx -k_2\left[\frac{k_1}{k_{-1}}[ThH][CO]\right]^2$$

where $k_2[ThCHO] \ll k_{-1}$ under the present conditions.[7]



(2)



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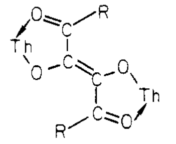
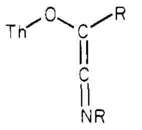


G



H

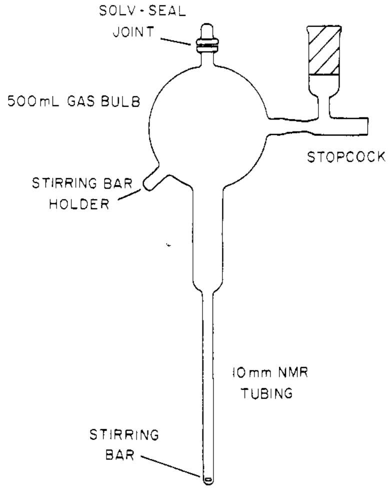
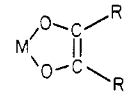
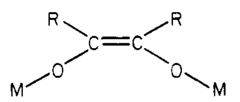


Figure 1. Reaction vessel.

migration in step d (e.g., eq 2 and 3[2a,10a,c,12]). This migration process is expected to be significantly accelerated by the γ-oxygen atom of E (Scheme I).[13] Furthermore, careful monitoring of 270-MHz ^1H spectra over the course of the coupling reaction gives no evidence for intermediates such as D or E. Carbene–CO coupling to form a ketene (schematically depicted as F, scenario 2) finds apparent precedent in reactions of actinide η^2-acyls with CO to yield dionediolates[2a,12] (G) and with isocyanides to yield ketenimines[12b,14] (H). Similar reactions are also known for transition-metal carbene complexes.[15] Judging from known thorium hydride[16] and organic ketene[17] chemistry, step g is likely to be fast compared to f; there is no spectral evidence for the presence of such a ketene intermediate during the course of the reaction. The kinetic treatment for scenario 2 predicts rate $\propto$ [ThH][CO]^2.[7,9b,18] Direct, bimolecular formyl dimerization (scenario 3) finds precedent in experimental and theoretical discussions of enediolate formation (e.g., I, J) during the carbonylation of actinide and early transition-metal hydrocarbyls.[2,3,19] The kinetic treatment[9c] predicts rate $\propto$ [ThH]^2[CO]^2.



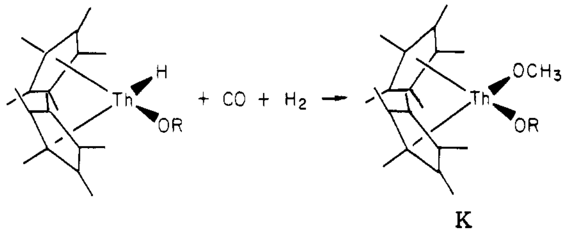
I



J

The rate of A → C conversion was measured via ^1H NMR for 0.06 M toluene-d_8 solutions of A (R = CH[C(CH$_3$)$_3$]$_2$) in the dark at 30 ± 0.4 °C. A specially designed reaction vessel (Figure 1) incorporating a 10-mm NMR tube, high vacuum connections, a 600-mL gas reservoir, and efficient stirring was employed to monitor the reaction rate as a function of [ThH] and CO pressure. Under these conditions, only A and C are detected and P_{CO} changes negligibly during the course of a kinetic run.[20] As can be seen in Figure 2A, the reaction at constant CO pressures is second order in thorium hydride over 3–4 half-lives and a ca. 5-fold CO pressure (which, in turn, is proportional to [CO] making the reasonable assumption that Henry's law is obeyed[18]) range. Furthermore, Figure 2B shows that the observed second-order rate constants are linearly proportional to the CO pressure; i.e., the reaction is first order in CO. These results are incompatible with scenarios 2 and 3 but are compatible with scenario 1. Linear regression analysis of these data yields k_2 = 0.31 (2) M^{-1} s^{-1}.

Additional support for scenario 1 and the intermediacy of a thoroxymethyl insertion intermediate (D) is provided by experiments designed to intercept such a species. When eq 1 is carried out under 6 atm of H_2 and 0.1 atm of CO, the major product (90%) is methoxide K (eq 4))[23] while the yield of C is reduced to 10%. Under these conditions, neither hydrogenation of enediolate C nor uncatalyzed



(4)

K

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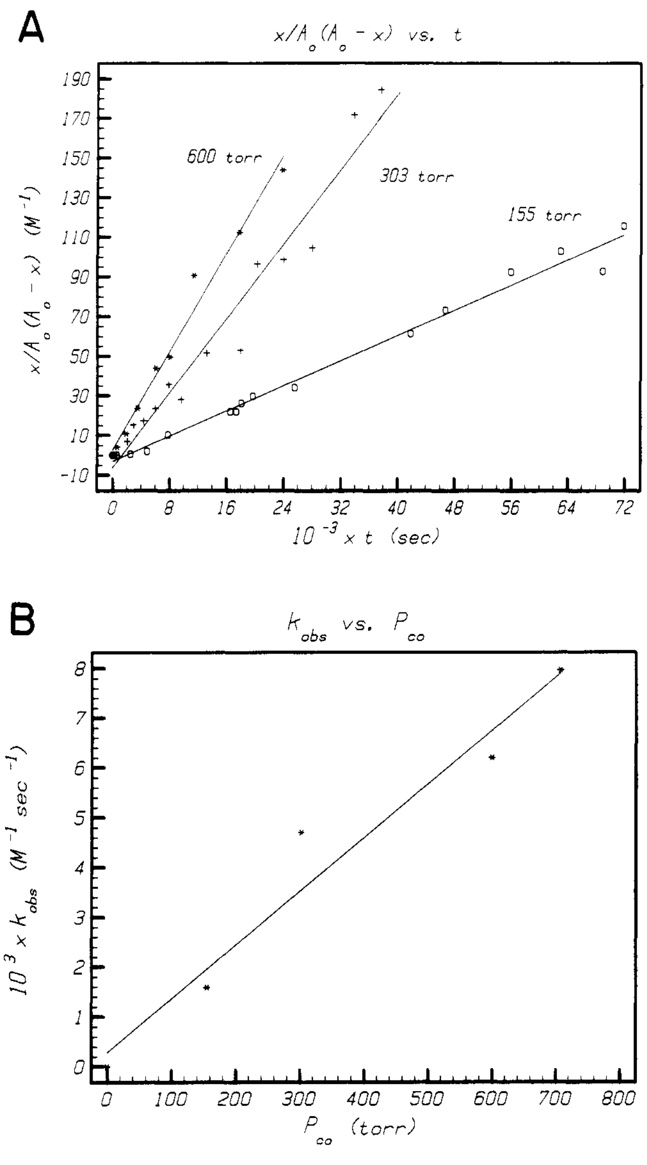
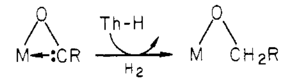


Figure 2. A. Kinetic plots for the reaction of $Th[(CH_3)_5C_5]_2\{OCH[C(CH_3)_3]_2\}H$ with CO at various constant CO pressures. B. Dependence of the observed rate constant on CO pressure.

hydrogenation[6] of thorium η^2-acyls occurs. Thus, eq 4 is readily understandable in terms of hydrogenolytic interception of D (Th–C bond hydrogenolysis is generally facile[6,16]) and is analogous to the final step in the thorium hydride catalyzed hydrogenation of actinide η^2-acyls (eq 5).[6]



(5)

In summary, the present kinetic and chemical evidence strongly implicate organoactinide formyls as key branch points in carbonylation processes which lead either to enediolates (CO–CO coupling) or to the production of methoxide functionalities (CO hydrogenation). Further efforts to quantify and manipulate these processes are in progress.

Acknowledgment. We thank the National Science Foundation (Grant CHE8009060) for generous support of this research.

Registry No. A (R = $CH[C(CH_3)_3]_2$, 79932-08-4; K (R = $CH[C(CH_3)_3]_2$, 83398-67-8.

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(20) In a Vacuum Atmospheres glovebox equipped with a recirculating Dri-Train, 2.5-mL portions of a 0.060 M solution of recrystallized $Th[(CH_3)_5C_5]_2\{OCH[C(CH_3)_3]_2\}H$[1a] in toluene-$d_8$ (dried over Na/K) were syringed into the NMR tube portion of the reaction vessel (Figure 1) which had previously been flamed under high vacuum (10^{-4} torr). The apparatus was then removed to a vacuum line and the thorium hydride solution freeze–thaw degassed. Next, the system was charged with the desired pressure of CO (passed through MnO and 4A molecule sieve columns[21]) by using a mercury U-tube manometer.[22] The vessel was next sealed and the solution-containing portion of the NMR tube placed in a 30 ± 0.4 °C thermostated bath, shielded from light. Rapid stirring was then initiated with a magnetic stirrer placed under the bath (control experiments established that under the present reaction conditions, variations in the stirring rate did not detectably affect the measured reaction rates).

Kinetic measurements were performed by quickly removing the reaction vessel from the constant temperature bath, transferring the stirring bar to the holding cup with a magnet, and inserting the NMR tube into the probe (30 °C) of a JEOL FX-90Q NMR spectrometer. The instrument had been previously tuned to maximize field homogeneity under nonspinning conditions. Proton spectra were recorded on disk under previously optimized conditions (nonspinning), the NMR tube removed from the probe, the stirring bar returned to the reaction solution, and the reaction vessel returned to the thermostated bath. Typically this operation required 2.0–2.5 min, and the kinetic results were found to be insensitive to whether this time was or was not included in the total reaction time. The kinetic measurements were typically carried out for 4 or more half-lives. Even for the lowest pressure CO run (155 torr), it was calculated that the CO pressure decreased by no more than 4% during the course of the run, ensuring that essentially constant concentrations of CO were maintained. The quantitative analysis consisted of integrating the Th–H resonance vs. the toluene-d_7 aromatic resonance as a function of time. Plots were fit by standard linear regression techniques, using a Hewlett-Packard HP1000-F data system and associated graphic peripherals.

(21) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* 1981, *103*, 6650–6667.

(22) (a) The vapor pressure of toluene under these conditions, ca. 20 torr,[22b] is relatively small and constant. (b) "CRC Handbook of Chemistry and Physics", 60th ed.; CRC Press: Boca Raton, FL, 1979; p D-209.

(23) An authentic sample was prepared by reaction of $Th[(CH_3)_5C_5]_2\{OCH[c(CH_3)_3]_2\}H$ with methanol: ^1H NMR (C_6D_6) δ 1.00 (s, 9H), 1.91 (s, 30 H), 3.68 (s, 1 H), 3.75 (s, 3 H); IR (Nujol mull, cm^{-1} 1390 (m), 1364 (m), 1113 (s), 1057 (s), 1009 (s), 960 (w), 919 (w), 765 (w), 722 (w), 656 (s). Anal. Calcd for $C_{30}H_{52}ThO_2$: C, 53.24; H,7.74. Found: C, 53.28; H,7.66.

An Alternate Binuclear Mechanism for Aldehyde Formation in the Reppe-Modified Hydroformylation Reaction[†]

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Summary: The isolable intermediates from the Reppe-modified hydroformylation reaction, $H^-Fe(CO)_4$ and $R^-Fe(CO)_4$, are shown to react together to provide aldehyde product. This result suggests that a binuclear intermediate may be responsible for aldehyde formation.

Elucidation of the primary mechanistic cycles involved in homogeneous reactions catalyzed by organotransition-metal complexes has required that attention be focused on the chemical reactivity of the supposed intermediates in these processes. In the course of such investigations, a number of binuclear reactions have been identified which

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[†] Dedicated to the memory of Professor Rowland Pettit