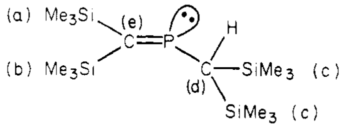
(DABCO) to form $(Me_3Si)_2C{=}PCl$[8] and (ii) treatment of $(Me_3Si)_2C{=}PCl$ with $(Me_3Si)_2CHLi$[9] in hexane solution. The overall yield of 4 (bp 79 °C at 0.005 torr) starting with $(Me_3Si)_2C{=}PCl$ was 75%. HRMS for 4: calcd 348.1710, found 348.1717; NMR data for 2: ^{13}C NMR (20 MHz) (Me_4Si) Me_3Si (a) δ 2.0 (d, $J_{PCSiC} = 5.4$ Hz), Me_3Si (b) δ 4.3 (d, $J_{PCSiC} = 3.1$ Hz), Me_3Si (c) δ 3.82 (s), PC (d) δ 40.6 (d, $J_{PC} = 87.3$ Hz), PC (e) δ 191 ($J_{PC} = 89.7$ Hz).



We next address the question of the mechanisms of formation of 3 and 4. Purification of the $[(Me_3Si)_2CH]_2PCl/Na$ reaction mixture by fractional vacuum distillation (bp 70–78 °C at 0.03 torr), followed by two recrystallizations from *n*-hexane at −20 °C, affords single crystals of the pure diphosphine $[(Me_3Si)_2CH]_4P_2$.[10] Dissolution of these crystals in *n*-hexane or toluene results in orange-red solutions which exhibit only one $^{31}P\{^1H\}$ NMR peak (+19 ppm (s)). Heating a toluene solution from +28 °C to +80 °C resulted in the gradual disappearance of the +19-ppm peak as the diphosphine 2 dissociated into the phosphinyl radical, 1. These changes were reversible, and no new peaks appeared. Furthermore, no new ^{31}P NMR peaks were detectable upon prolonged storage of *n*-hexane solutions of 1/2 mixtures at 25 °C. Clearly, 3 and 4 are not produced via the phosphinyl radical, 1, or the diphosphine, 2. To shed more light on this question, an *n*-hexane solution of the 1/2 radical/diphosphine mixture was treated with an equimolar quantity of Na at 65 °C for 14 h. This resulted in the complete consumption of 1 and 2 and the formation of a 60/40 mixture of 3 and the new phosphide anion $[\{(Me_3Si)_2CH\}_2P]^-$ (5) (^{31}P chemical shift, −106 ppm). This experiment suggests that in the $[(Me_3Si)_2CH]_2PCl/Na$ coupling reaction, 3 arises via the phosphide anion, 5. Interestingly, the phosphide anion, 5, is not produced by treatment of the secondary phosphine, 3, with *n*-BuLi, *n*-BuLi/TMEDA, MeLi, or KH, presumably because of the steric bulk of the $(Me_3Si)_2CH$ ligand.

Considering that the phosphaalkene 4 might be produced by dehydrochlorination of $[(Me_3Si)_2CH]_2PCl$, we treated this compound with DABCO in ether solution for 4 h at 40 °C. However, the chlorophosphine failed to react and was recovered quantitatively. Further experimentation will therefore be necessary to reveal the mechanism of phosphaalkene formation.

The coordination chemistry of the phosphide anion, 5, is under active investigation.

Acknowledgment. We are grateful to NATO, the National Science Foundation, the Robert A. Welch Foundation, and SERC for generous financial support.

Registry No. 1, 63429-86-7; 2, 83436-91-3; 3, 83436-92-4; 4, 83436-93-5; 5, 83436-94-6; $[(Me_3Si)_2CH]_2PCl$, 63429-87-8.

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[8] This compound was described first by Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, *22*, 2159–2160.

[9] Preparation of $(Me_3Si)_2CHLi$ and thus other $(Me_3Si)_2CH$-substituted compounds is greatly facilitated by our "one-pot" synthesis of $(Me_3Si)_2CHCl$: Cowley, A. H.; Kemp, R. A. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 591–595.

[10] The structures of $[(Me_3Si)_2CH]_4P_2$ and $[\{(Me_3Si)_2CH\}_2P]\cdot$ have been determined recently by X-ray crystallography and gas-phase electron diffraction, respectively. This work will be published in a separate manuscript.

Steric Effects of Phosphido Ligands. Synthesis and Crystal Structure of Di-*tert*-butylphosphido-Bridged Dinuclear Metal–Metal Bonded Complexes of Fe(II), Co(I, II), and Ni(I)[†]

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Summary: Reaction of $t\text{-}Bu_2PLi$ with $MCl_2(PMe_3)_2$ (M = Fe, Co, Ni) in THF at −78 °C yields $[Fe(\mu\text{-}t\text{-}Bu_2P)Cl(PMe_3)]_2$ (1), $Co_2(\mu\text{-}t\text{-}Bu_2P)_2Cl(PMe_3)_2$ (2), and $[Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (3) whose structures have been determined by X-ray diffraction studies.

It is well-known that variation in the size of the R groups of trialkyl- or triarylphosphines (PR_3) can dramatically alter the chemical and physical properties of their transition-metal complexes.[1] However, similar studies of transition-metal phosphido complexes are not available as most of them are derivatives of diphenyl (Ph_2P^-) or dimethyl (Me_2P^-) phosphide which are not particularly bulky.[2]

As part of a program aimed at the study of steric effects in transition-metal phosphido complexes we have initially studied the chemistry of the di-*tert*-butylphosphido ($t\text{-}Bu_2P^-$) unit. At present there are only three other d-block transition-metal complexes containing this unit, and none has been structurally characterized.[3] Apart from a few phosphine-stabilized phosphido complexes of the nickel triad[2] most phosphido complexes of the transition metals have either $\eta^5\text{-}C_5H_5$, CO, or NO as ancillary ligands.[2]

We have, therefore, initially examined the reaction of the late first-row metal phosphine halides $MCl_2(PR_3)_2$ (M = Fe, Co, Ni; R = Me) with $Li\text{-}t\text{-}Bu_2P$ in order to prepare a range of phosphido complexes with trialkylphosphines as stabilizing ligands.

The reaction of $MCl_2(PMe_3)_2$ (M = Fe,[4] Co,[5] Ni[6]) with 2 molar equiv of $Li\text{-}t\text{-}Bu_2P$[7] in tetrahydrofuran at −78 °C yields $[Fe(\mu\text{-}t\text{-}Bu_2P)Cl(PMe_3)]_2$ (1), $Co_2(\mu\text{-}t\text{-}Bu_2P)_2Cl(PMe_3)_2$ (2) and $[Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (3)[8] (Scheme I).

[†] Dedicated to the memory of Rowland G. Pettit.

[1] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[2] See, for reviews: Hayter, R. G. *Prep. Inorg. React.* **1965**, *2*, 211. Robinson, S. D. *MTP Int. Rev. Sci. Part 2* **1976**, *6*, 133. See also: Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 331 for the use of the bridging $\{[(Me_3Si)_2CH]_2P\}\cdot$ radical.

[3] Schumann, H.; Neumann, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 708; $[M(CO)_4(\mu\text{-}t\text{-}Bu_2P)]_2$, M = Mn, Re. Schumann, H.; Heisler, M. *Chem. Ber.* **1979**, *112*, 541; $Rh_2(CO)_2Cl(P\text{-}t\text{-}Bu_3)_2(\mu\text{-}t\text{-}Bu_2P)$.

[4] Karsch, H. H. *Chem. Ber.* **1977**, *110*, 2222.

[5] Jensen, K. A.; Nielsen, P. H; Petersen, C. T. *Acta Chem. Scand.* **1963**, *17*, 1115.

[6] Dahl, O. *Acta Chem. Scand.* 1969, *23*, 2342.

[7] Hoffman, H.; Schellenbeck, P. *Chem. Ber.* **1966**, *99*, 1134. Issleib, K.; Krech, F. *J. Organomet. Chem.* **1968**, *13*, 283.

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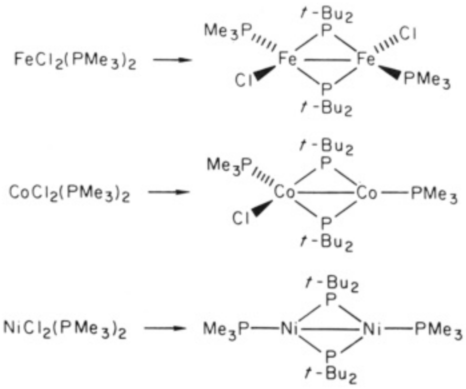
Scheme I[a]



[a] See ref 8 for conditions.

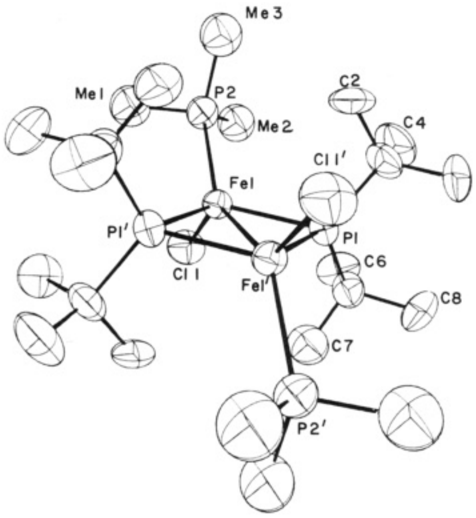


Figure 1. View of $[Fe(\mu\text{-}t\text{-}Bu_2P)Cl(PMe_3)]_2$ (**1**), molecule 1. Important bond lengths (Å): Fe–Fe = 2.840 (3), Fe(1)–P(1) = 2.363 (5), Fe(1)–P(2) = 2.478 (5), Fe(1)–Cl(1) = 2.281 (5). Bond angles (deg): Fe(1)–P(1)–Fe(1′) = 73.7 (2), P(1)–Fe(1)–P(1′) = 106.3 (2), P(2)–Fe(1)–Cl(1) = 88.8 (2), P(1)–Fe(1)–Cl(1) = 113.0 (2), P(1)–Fe(1)–P(2) = 118.5 (2), Fe(1)–P(1)–C(1) = 118.3 (6), C(1)–P(1)–C(5) = 111.7 (8).

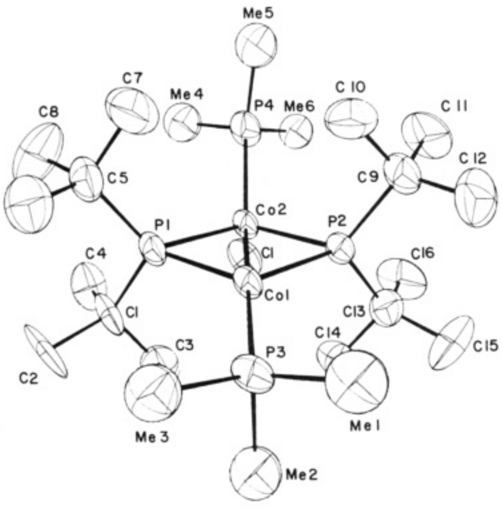


Figure 2. View of $Co_2(\mu\text{-}t\text{-}Bu_2P)_2Cl(PMe_3)_2$ (**2**). Important bond lengths (Å): Co–Co = 2.508 (2), Co(1)–P(1) = 2.180 (4), Co(2)–P(1) = 2.324 (4), Co(1)–P(3) = 2.174 (4), Co(2)–P(4) = 2.320 (4), Co(2)–Cl(1) = 2.276 (4). Bond angles (deg): Co(2)–P(1)–Co(1) = 67.6 (1), P(1)–Co(1)–P(2) = 117.4 (2), Co(2)–Co(1)–P(3) = 168.3 (1), P(4)–Co(2)–Cl(1) = 90.5 (2).

Complexes **1**, **2**, and **3** are red-brown, crystalline, petroleum-soluble, and moderately air sensitive. Their structures have been determined by X-ray diffraction studies.[9] Views of **1**, **2**, and **3** are shown in Figures 1, 2, and 3, respectively. There are several noteworthy features of the new complexes isolated, and our initial studies suggest that the chemistry of phosphido ligands with bulky substituents will have a rich and interesting chemistry which is significantly different from those of either Ph_2P^- or Me_2P^-.

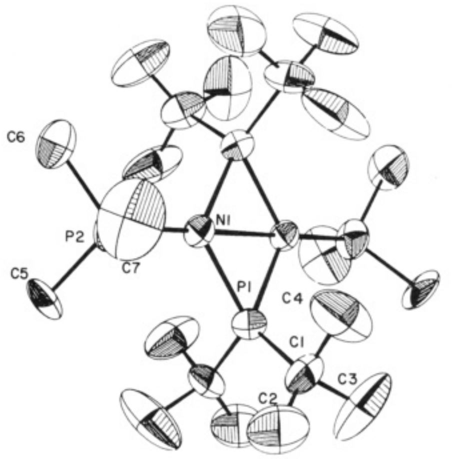


Figure 3. View of $[Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (**3**). Important bond lengths (Å): Ni–Ni = 2.375 (3), Ni–P(1) = 2.174 (3), Ni(1)–P(2) = 2.136 (5). Bond angles (deg): Ni–P(1)–Ni′ = 66.2 (1), Ni–Ni–P(2) = 180.000 (0), P(1)–Ni–P(2) = 123.12 (6).

Notable features are the following. (i) Stabilization of a d^6 iron(II) dimer in which the structure can be considered to consist of two distorted Fe(II) tetrahedra held together by $\mu\text{-}t\text{-}Bu_2P$ bridges: Tetrahedral Fe(II) d^6 is quite rare,[10]

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(8) In a typical reaction a solution of Li-t-Bu_2P (10.64. mmol, 11.93 mL of a 0.892 M THF solution) is added to a suspension of $MCl_2(PMe_3)_2$ (5.32 mmol) in THF (100 mL) at −78 °C. The mixture is allowed to warm slowly to room temperature (1.5 h), and volatile materials are removed under vacuum. The residue is extracted with hexane (2 × 25 mL) and the solution filtered and evaporated to ca. 15 mL under vacuum. Cooling (−20 °C) yields red-brown crystals of the complexes that are collected and dried under vacuum. Yields: **1**, 5%; **2**, 25%; **3**, 60%. The compounds all gave satisfactory elemental analyses (C, H, P). Melting points: **1**, 101–105 °C dec; **2**, 330–335 °C dec; **3**, 183–185 °C dec. ^1H NMR data (**3**) in C_6D_6: δ 1.50 (mult overlapping PMe_3 and t-Bu–P) resonances), relative to Me_4Si at δ 0.0, at ambient temperature and 90 MHz. $^{31}P\{^1H\}$ NMR: δ 171.03 (t, t-BuP), 23.11 (t, PMe_3, $^2J_{P-P} = 30.0$ Hz), relative to external 85% H_3PO_4 at δ 0.0, at 32.384 MHz and ambient temperature.

(9) Crystal Data for $Fe_2P_4Cl_2C_{22}H_{54}$ (**1**): monoclinic, space group $P2_1/c$, $M_r = 625.2$, $a = 15.753$ (8) Å, $b = 15.875$ (8) Å, $c = 13.544$ (6) Å, $\beta = 94.69$ (2)°, $U = 3375.7$ Å^3, $D_{calcd} = 1.23$ g cm^{-3}, $Z = 4$ (dimers), $F(000) = 1328$, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 12.3 cm^{-1}. The final R factor based on 1487 observed reflections was 0.072. There were two independent molecules in the asymmetric unit, each residing on a crystallographic center of inversion. A view of molecule 1 is seen in Figure 1. The bonding parameters for the two molecules were very similar. For molecule **2** bond lengths (Å): Fe–Fe = 2.805 (3), Fe(2)–P(3) = 2.347(5), Fe(2)–P(4) = 2.449 (5), Fe(2)–Cl(2) = 2.276 (5). Bond angles (deg): Fe(2)–P(3)–Fe(2′) = 73.2(2), P(3)–Fe(2)–P(3′) = 106.8(2), P(4)–Fe(2)–Cl(2) = 89.0 (2), P(3)–Fe(2)–Cl(2) = 113.1 (2), P(3)–Fe(2)–P(4) = 115.8 (2), Fe(2)–P(3)–C(9) = 121.7 (6), C(9)–P(3)–C(13) = 110.5 (8). Crystal Data for $Co_2P_4ClC_{22}H_{54}$ (**2**): monoclinic, space group $P2_1/n$, $M_r = 596.0$, $a = 10.776$ (5) Å, $b = 18.909$ (8) Å, $c = 16.217$ (7) Å, $\beta = 104.30$ (3)°, $U = 3202.0$ Å^3, $D_{calcd} = 1.24$ g cm^{-3}, $Z = 4$ (dimers), $F(000) = 1268$, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 13.6 cm^{-1}. The final R factor based on 1815 observed reflections was 0.065. A view of the molecule is presented in Figure 2. Crystal Data for $Ni_2P_4C_{22}H_{54}$ (**3**): tetragonal, space group $P\overline{4}n2$, $M_r = 560.0$, $a = 9.300$ (4) Å, $c = 18.402$ (8) Å, $U = 1591.6$ Å^3, $D_{calcd} = 1.17$ g cm^{-3}, $Z = 2$ (dimers), $F(000) = 604$, γ(Mo Kα) = 0.710 69 Å^3, μ(Mo Kα) = 13.9 cm^{-1}. The final R factor based on 463 observed reflections was 0.037. A view of the molecule is presented in Figure 3. All three data crystals were sealed under vacuum in 0.5-mm o.d. Lindemann glass capillaries. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The diffracted intensities were collected by the (ω–2θ) scan technique as described in: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

(10) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 756.

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-*t*-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-*t*-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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(11) See, for example: Ginsburg, R. E.; Berg, J. M.; Rothrock, R. K.; Collman, J. P.; Hodgson, K. O.; Dahl, L. F. *J. Am. Chem. Soc.* **1979,** *101,* 7218 and references therein.

(12) Albright, T. A., private communication.

(13) Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975,** 2410.

(14) Reed, J.; Schultz, A. J.; Pierpont, C. G.; Eisenberg, R. *Inorg. Chem.* **1973,** *12,* 2949.

(15) Mason, R.; Sotofte, I.; Robinson, S. D.; Uttley, M. F. *J. Organomet. Chem.* **1972,** *46,* C61.

(16) See: Burdett, J. K. *J. Chem. Soc., Dalton Trans.* **1977,** 423 for references to other Fe–Fe bonds. See also: Summerville, R. H.; Hoffman, R. *J. Am. Chem. Soc.* **1976,** *98,* 7240 for theoretical calculations.

(17) See, for example: Brown, D. B., "Mixed Valence Compounds"; D. Reidel Publishing Co: Boston, MA, 1980.

(18) Schäfer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979,** *34B,* 1358. See ref 4 for $[Ni(PR_3)(P(SiMe_3)_2]_2$. See also: Nobile, C. F.; Vasapollo, G.; Giannoccaro, P.; Sacco, A. *Inorg. Chim. Acta* **1981,** *48,* 261 for $[Ni(\mu\text{-}P\text{-}c\text{-}Hx_2)(P\text{-}c\text{-}Hx_2Ph)]_2$.

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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