the *syn* tetraol derivative **7** with excellent stereoselectivity. The double 1,2-Wittig rearrangement of **8** provided **9** in low yield but with the expected *syn* selectivity.[11,14]

In order to differentiate the vinyl groups present in **4**, a chiral, nonracemic reagent or catalyst must be employed. As in the earlier study, we have examined the Sharpless asymmetric epoxidation reaction for this purpose.[2] Like the simple divinyl carbinols, **4** undergoes epoxidation with group and face selectivity with the *pro*-S and *pro*-R selective Sharpless reagents to provide either **10**[15] ($[\alpha]^{25}_{\mathrm{D}}$ −0.86°, *c* 1.51, $CHCl_3$) or **11** ($[\alpha]^{25}_{\mathrm{D}}$ +0.80°, *c* 1.50, $CHCl_3$), respectively. The minor enantiomers produced in these reactions are selectively "destroyed" by a fast second epoxidation reaction (kinetic resolution). Accordingly, the enantiomeric excess increases as the reaction proceeds to completion; with substrates such as **4**, **9**, and **12** we expect extremely high levels of enantiomeric purity to be obtained (ee > 99.99999).[2] The *pro*-S selective reagent converts **12**[16] into **13** and **9** into **14** in excellent yield and enantioselectivity. It is interesting to note that the reaction determines the absolute stereochemistry at six and seven stereocenters in **13** and **14**, respectively. Since both Sharpless reagents are available, advanced meso synthetic intermediates such as **9** can now be converted into either of two antipodal products.

Compound **14** has been converted to the all *syn* hexaol derivative **15** by the transformations depicted in Scheme IV. On comparison with the degradation product **1**, it is clear that these substances have an *isomeric* relationship. Consequently, we conclude that mycoticin A does not contain the all *syn* polyol configuration.[17] It is apparent that the assumptions concerning the common biogenesis of members of this class require reevaluation.

In summary, enantiotopic group selective reactions are capable of converting achiral, meso compounds into either of two antipodal products and with enhanced levels of enantiomeric purity.[18] These reactions provide a solution to the problem of terminus differentiation presented by the two-directional synthesis strategy that utilizes achiral (class A)[1] chains.[19] The present illustration resulted in the enantioselective formation of *syn*-skipped polyol chains. A report on further investigations concerning the stereochemistry of mycoticin A will be forthcoming.

**Acknowledgment.** These investigations were supported by the NIH, NSF (Presidential Young Investigator Award), Alfred P. Sloan Foundation (1985–87), and The Camille and Henry Dreyfus Foundation, Inc. (Teacher/Scholar Award 1984–89) to whom we are grateful. Matching funds for the NSF/PYI Award were generously provided by Berlex Co., Stuart Pharmaceuticals, and Pfizer, Inc. We thank Zhaoyin Wang for stimulating discussions that helped catalyze these investigations.

**Supplementary Material Available:** X-ray crystallographic and spectral data and degradation scheme (25 pages). Ordering information is given on any current masthead page.

---

(13) (a) Muxfeldt, H.; Haas, G.; Hardtmann, G.; Kathawala, F.; Mooberry, J. B.; Vedejs, E. *J. Am. Chem. Soc.* **1979**, *101*, 689. (b) Stork, G.; Paterson, I.; Lee, F. K. C. *J. Am. Chem. Soc.* **1982**, *104*, 4686.

(14) The low yields associated with the 1,2-Wittig rearrangement make this reaction unattractive in a preparative sense. In the present study, the application of this transformation in two directions provided ready access to sufficient quantities of materials to allow for structural comparison with naturally derived substances. In theory, any synthesis of *syn* 1,3-diols that relies solely on internal asymmetric induction can be conducted simultaneously in two directions.

(15) The stereochemistry of **10** was supported by the X-ray crystallographic structure determination of the corresponding bisacetate. Details are available in the Supplementary Material.

(16) Prepared from **4** according to the sequence: (a) TBSCl, imidazole, $CH_2Cl_2$ (94%); (b) i. $O_3$, $CH_2Cl_2$; ii. $(Ph)_3P$, room temperature, iii. triethyl phosphonoacetate, NaH, 0 °C (80%); (c) DIBAL, $CH_2Cl_2$ (91%); (d) BnBr, NaH, DMF (90%); (e) tetrabutylammonium fluoride, THF (96%).

(17) The *anti* relationship depicted between the $C_2$ methyl and $C_3$ oxygen substituents of **1** has been established from degradation studies of mycoticin A (unpublished results).

(18) For an example of terminus differentiation of a meso chain, see: Mohr, P.; Waespe-Sarcevic, N.; Tamm, C.; Gawronska, K.; Gawronska, J. K. *Helv. Chim. Acta* **1983**, *66*, 2501.

(19) An early application of the two-directional strategy suffered only at this late stage task, see: Still, W. C.; Barrish, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 2487.

## Reductive Elimination Pathways to Low-Valent Titanium Aryloxide Complexes

Loren D. Durfee, Phillip E. Fanwick, and Ian P. Rothwell*[1]

*Department of Chemistry, Purdue University*
*West Lafayette, Indiana 47907*

Kirsten Folting and John C. Huffman

*Molecular Structure Center, Indiana University*
*Bloomington, Indiana 47405*

*Received March 16, 1987*

The lower valent compounds of titanium have been associated with a wide range of inorganic and organometallic reactivity.[2] In particular the reduction of titanium alkoxides[3] and phenoxides[4] has been reported to lead to a number of very reactive but difficult to characterize titanium(II) derivatives, some of which have the ability to coordinate and activate dinitrogen.[3-5] However, to date there has been no report of a well-characterized titanium(II) alkoxide or phenoxide in the literature. We wish to report here the generation of a number of Ti(II) and Ti(III) aryloxide compounds by ligand induced reductive–elimination pathways from a Ti(IV) organometallic compound.[6]

The mono-$\eta^2$-iminoacyl compound Ti(OAr-2,6-*i*-Pr$_2$)$_2$($\eta^2$-*t*-BuNCCH$_2$Ph)(CH$_2$Ph) (**1**)[7] will react smoothly over a period of hours with pyridine (≥1 equiv) in hydrocarbon solvents to produce the $\eta^2$-imine compound Ti(OAr-2,6-*i*-Pr$_2$)$_2$[$\eta^2$-*t*-BuNC(CH$_2$Ph)$_2$](py) (**2a**) (Scheme I).[8] A single-crystal X-ray diffraction study of the 4-phenylpyridine derivative (**2b**)[9] confirmed

---

(1) Camille and Henry Dreyfus Teacher-Scholar, 1985–1990 and Fellow of the Alfred P. Sloan Foundation, 1986–1990.

(2) (a) *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E.; Eds.; Pergamon Press: Oxford, 1982; Vol. 3, Chapter 22.2 and references therein. (b) Wailes, P. C.; Coults, R. S. P.; Weigold, H., *Organometallic Chemistry of Titanium, Zirconium and Hafnium*; Academic Press: New York, 1974.

(3) Van Tamelen, E. E. *Acc. Chem. Rev.* **1970**, *3*, 361 and references therein.

(4) Flamini, A.; Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 454.

(5) See, also: Sanner, R. D.; Duggon, D. M.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358 and references therein.

(6) Carbonylation of titanocene dialkyls has been shown to lead to $Cp_2Ti(CO)_2$ with the elimination of ketones, via $\eta^2$-$R_2CO$ complexes which can sometimes be isolated, see: (a) Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*; 668 and references therein. (b) Fachinetti, G.; Floriani, C. *J. Am. Chem. Soc.* **1961**, *83*, 1287. (c) Demerseman, L. B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1977**, *132*, 223.

(7) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Strieb, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390.

(8) Addition of pyridine (py, ≥1 equiv) to a solution of Ti(OAr-2,6-i-Pr$_2$)$_2$($\eta^2$-*t*-BuNCCH$_2$Ph)(CH$_2$Ph)(1.9 g, 2.8 mmol) in benzene (30 mL) results in the formation of **2a** over 90 min. Removal of benzene solvent in vacuo followed by addition of hexane gave the product as a red-brown solid in essentially quantitative yield. The 4-phenylpyridine derivative **2b** was obtained via an identical procedure, and X-ray quality crystals were obtained from hexane on slow cooling. Anal. Calcd for $TiC_{48}H_{62}N_2O_2$ (**2a**): C, 77.18; H, 8.37; N, 3.75. Found: C, 75.92; H, 8.48; N, 3.40. Anal. Calcd for $TiC_{54}H_{66}O_2N_2$ (**2b**): C, 78.80; H, 8.08; N, 3.40. Found: C, 79.52; H, 8.41; N, 3.51. Selected spectroscopic data: $^1$H NMR ($C_6D_6$, 30 °C) (2a) $\delta$ 3.63 (d), 3.77 (d, C*H*$_2$Ph), 1.30 (s, C*Me*$_3$), 3.73 (septet, C*H*Me$_2$), 1.16 (d), 1.19 (d, CH*Me*$_2$), (**2b**) $\delta$ 3.83 (d), 3.95 (d, C*H*$_2$Ph), 1.44 (s, C*Me*$_3$), 3.88 (septet C*H*Me$_2$), 1.28 (d), 1.35 (d, CH*Me*$_2$). $^{13}$C NMR ($C_6D_6$, 30 °C) (**2a**) $\delta$ 95.0 (N*C*), 47.0 (*C*H$_2$Ph), 64.1 (*C*Me$_3$), 32.5 (C*Me*$_3$), (**2b**) $\delta$ 96.8 (N*C*), 47.2 (*C*H$_2$Ph), 64.2 (*C*Me$_3$), 32.6 (C*Me*$_3$).

(9) Crystal data for $TiO_2N_2C_{54}H_{66}$ (**2b**) at −155 °C: space group $P2_1/c$, $a = 12.970$ (4) Å, $b = 12.927$ (3) Å, $c = 28.140$ (4) Å, $\beta = 97.38$ (2)°, $Z = 4$, $d_{\mathrm{calcd}} = 1.168$ g cm$^{-3}$. Of the 6427 unique data collected by using Cu K$\alpha$ radiation, $3° \leq 2\theta \leq 112°$, the 3514 with $F > 3\sigma(F)$ were used in the final refinement. Final residuals are $R = 0.051$, $R_w = 0.068$.

0002-7863/87/1509-4720$01.50/0

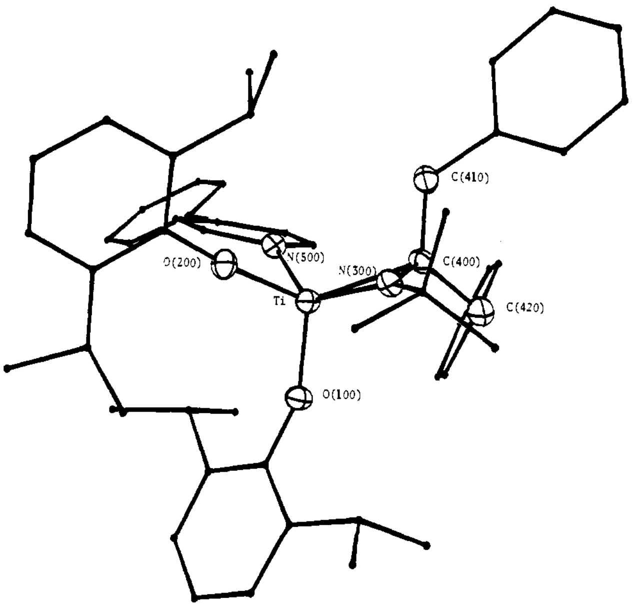
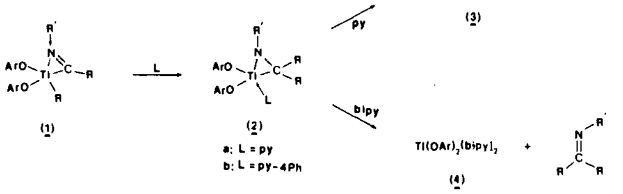


**Figure 1.** ORTEP view of **2b** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (°): Ti–O(100) = 1.848 (3); –O(200) = 1.829 (4); –N(300) = 1.846 (4); –N(500) = 2.216 (5); –C(400) = 2.158 (5); N(300)–C(400) = 1.421 (7); N(300)–Ti–C(400) = 40.6(2).

**Scheme I**



the formulation as well as the presence of the aza-metallacyclopropane ring formed by the ligand-induced migration of the benzyl group to the $\eta^2$-iminoacyl.[10] Figure 1 shows an ORTEP view of **2b** along with some important bond distances and angles. The spectroscopic properties of **2**[8] are consistent with this observed solid-state structure, in particular the equivalent benzyl groups are seen to contain diastereotopic methylene protons in the $^1$H NMR while the diastereotopic methyl groups of the OAr-2,6-*i*-$Pr_2$ ligands are as expected for a tetrahedral M(OAr-2,6-*i*-$Pr_2$)$_2$(X)(Y) molecule.[7]

Reaction of **2** with excess of pyridine in hexane results in the darkening of the solution over hours and formation of a deep purple crystalline precipitate **3**. Microanalytical data on **3** suggested the possible stoichiometry [Ti(OAr-2,6-*i*-$Pr_2$)$_2$(py)$_3$][11] while analysis ($^1$H NMR) of the supernatant showed the presence of the eliminated imine, $(PhCH_2)_2C{=}N$-*t*-Bu and its enamine tautomer (Scheme I).[12] An X-ray diffraction study of sparingly soluble **3**[13] (Figure 2) showed the presence of a dimer, formed by the

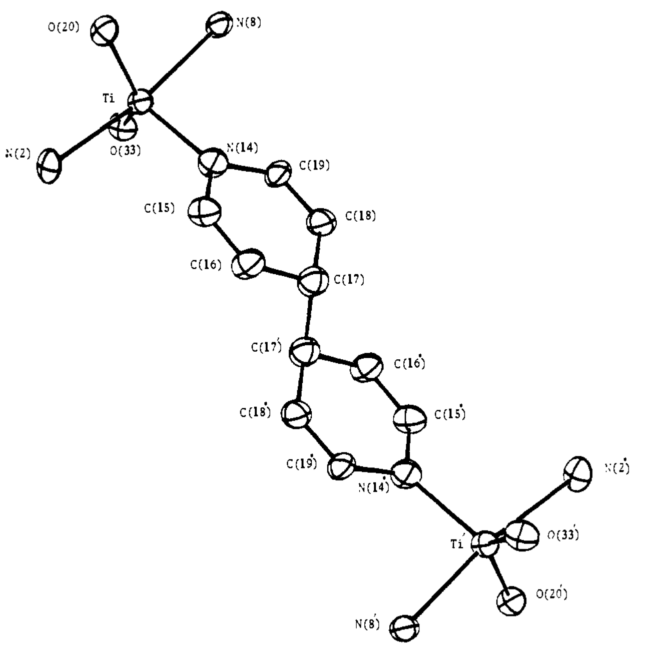


**Figure 2.** ORTEP view of **3**, showing only the metal coordination spheres and coupled pyridine bridge. Some selected bond distances (Å) and angles (°): Ti–O(20) = 1.883 (7); –O(33) = 1.891 (7); –N(2) = 2.237 (9); –N(8) = 2.235 (9) (a); –N(14) = 2.012 (9); O(20)–Ti–O(33) = 133.6 (3); –N(2) = 86.8 (3); –N(8) = 87.3 (3); –N(14) = 114.7 (4); O(33)–Ti–N(2) = 87.5 (3); –N(8) = 92.2 (3); –N(14) = 111.8 (4); N(2)–Ti–N(8) = 171.5 (3); –N(14) = 96.2 (14); –N(8)–Ti–N(14) = 91.8 (3).

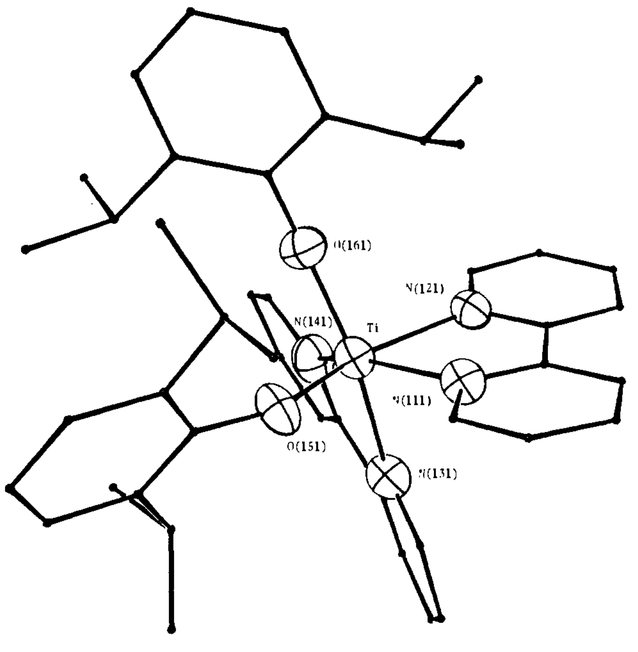


**Figure 3.** ORTEP view of molecule 1 in the unit cell of **4**. Selected bond distances (Å) and angles (°): Ti(1)–O(151) = 1.896 (6); –O(161) = 1.882 (6); –N(111) = 2.167 (6); –N(121) = 2.201 (7); –N(131) = 2.159 (7); –N(141) = 2.129 (7); O(151)–Ti(1)–O(161) = 94.0 (3). Distances and angles in molecule 2 are essentially identical.

---

[10] Although similar $\eta^2$-imine complexes have been proposed for a number of early and late transition metals, only one example (ref a) has been previously characterized crystallographically, see: (a) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 2088. (b) Mayer, J. M.; Curtis, C. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651. (c) Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450. (d) Takahashmi, Y.; Onoyama, N.; Ishikawa, Y.; Motojima, S.; Sugiyama, K. *Chem. Lett.* **1978**, 525. (e) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1203. (f) Browning, J.; Empsall, H. D.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 381.

[11] Addition of pyridine (0.24 mL, 3.0 mmol) to a hexane (20 mL) solution of Ti(OAr-2,6-i-$Pr_2$)$_2$($\eta^2$-*t*-BuNCC$H_2$Ph)(C$H_2$Ph) (0.5 g, 0.75 mmol) resulted in a slow darkening of the solution. After 15 h the resulting deep red solution was decanted away from the dark-red needlelike precipitate of **3**. Yield = 0.30 g (64%). Accurate microanalytical data on **3** has proved very difficult to obtain. Anal. Calcd for $TiC_{39}H_{49}N_3O_2$: C, 73.20; H, 7.72; N, 6.57. Found: C, 69.47; H, 7.74; N, 5.83.

[12] $^1$H NMR ($C_6D_6$, 30 °C): δ 1.33 (s, C=N-*t*-*Bu*), 2.8 (br, N*H*), 3.60 (s, PhHC=C(C*H*$_2$Ph)NH-*t*-Bu), 5.85 (s, Ph*H*C=C). See: Clark, R. A.; Parker, D. C. *J. Am. Chem. Soc.* **1971**, *93*, 7257.

reductive coupling of pyridine ligands through the 4-position in the intermediate Ti(II) complex.[14] This results in a final oxidation state of 3+ for the titanium atoms in **3**. The much shorter distance to the reduced pyridine ring nitrogen is consistent with the resulting amido linkage.

The use of the more redox stabilizing 2,2′-bipyridyl (bipy) ligand allows the isolation of the more soluble deep blue-green derivative $Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(bipy)_2$ (**4**) directly from **2** (Scheme I).[15] An X-ray diffraction study of **4**[16] confirms the stoichiometry and shows the aryloxide ligands to be mutually cis (Figure 3). Electrochemical studies of **4** show the presence of two one-electron oxidations at –0.95 and –0.07 V as well as a one-electron reduction at –1.51 V. All three waves appear to be reversible as judged by the ratio's $I_a/I_c = 1$. indeed, bulk electrochemical oxidation at –0.75 V generates stable, olive-green solutions of the monocation $[Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(bipy)_2]^+$[18] which exhibits an identical cyclic voltammogram to solutions of **4** except that the wave at –0.95 V is now a reduction. However, attempts to generate solutions of the ions $[Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(bipy)_2]^{2+}$ and $[Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(bipy)_2]^-$ by bulk electrochemical oxidation at +0.0 V and reduction at –1.7 V led to solutions having broad cyclic voltammograms with no relationship to those of **4**. The electrochemical and spectroscopic properties so far examined for **4** are consistent with its formulation as containing a Ti(II) metal center and against an alternate formulation as $[Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(bipy^-)(bipy)]$ although further studies are presently underway on **4** and other related derivatives to more fully establish this point.

**Acknowledgment.** We thank the National Science Foundation (Grant CHE-8612063) for support of this research. I.P.R gratefully acknowledges the Camille and Henry Dreyfus Foundation for the award of a Teacher-Scholar Grant as well as the Alfred P. Sloan Foundation for the award of a Fellowship. L.D.D. expresses his appreciation to Amoco for the award of a Fellowship.

**Supplementary Material Available:** Tables of atomic coordinates, temperature factors, and bond distances and angles (40 pages); tables of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

---

(13) Crystal data for $Ti_2O_4N_6C_{78}H_{98}$ (**3**) at –156 °C: space group $P\bar{1}$, $a = 14.557$ (7) Å, $b = 13.155$ (7) Å, $c = 11.507$ (6) Å, $\alpha = 101.83$ (2)°, $\beta = 86.02$ (2)°, $\gamma = 107.86$ (2)°, $Z = 1$, $d_{calcd} = 1.035$ g cm$^{-3}$. Of the 5402 unique reflections collected by using Mo K$\alpha$ radiation, $6° \leq 2\theta \leq 45°$, the 2777 were used in the final refinement. Final residuals are $R = 0.0789$, $R_W = 0.0826$. A disordered molecule of solvent was located in the unit cell, but it proved impossible to identify its chemical nature.

(14) (a) Dorogy, W. E.; Schram, E. P. *Inorg. Chim. Acta* **1983**, *73*, 31 and references therein. (b) Birch, A. J.; Karakhanov, E. A. *J. Chem. Soc., Chem. Commun.* **1975**, 480.

(15) To a solution of **2a** (0.43 g, 0.58 mmol) in benzene (30 mL) was added 2 equiv of bipy (0.18 g, 1.2 mmol). The solution rapidly turned from red-brown in color to dark blue-green. After 30 min the solvent was removed in vacuo, and the remaining solids were washed with hexane. Yield = 0.33 g (80%). Quality crystals were obtained from toluene on slow cooling. Anal. Calcd for $TiC_{44}H_{50}O_2N_4$: C, 73.93; H, 7.05; N, 7.84. Found: C, 72.33; H, 7.21; N, 7.31.

(16) Crystal data for $TiO_2N_4C_{44}H_{50}$ (**4**) at 22 °C: space group $P\bar{1}$, $a = 13.102$ (4) Å, $b = 16.328$ (4) Å, $c = 19.726$ (3) Å, $\alpha = 102.57$ (2), $\beta = 96.54$ (2), $\gamma = 102.06$ (2), $Z = 4$, $d_{calcd} = 1.195$ g cm$^{-3}$. A total of 10 347 unique data were collected with Mo K$\alpha$ $4° \leq 2\theta \leq 45°$ of which 5767 with $F > 3\sigma(F)$ were used in the refinement. Two similar but independent molecules were found in the unit cell. The data reported here is for the present state of refinement with only the central coordination sphere anisotropic giving residuals of $R = 0.089$ and $R_W = 0.122$. Further refinement is presently underway.

(17) Cyclic voltammograms and bulk electrochemistry were performed by using a Bioanalytical Systems Inc. Model CV-27 instrument, a three compartment H-cell, 0.2 M $n\text{-}Bu_4N^+PF_6^-$/THF solvent, Pt-disk or gauze electrode, and a Ag/AgCl quasi-reference electrode against which the $Cp_2Fe/Cp_2Fe^+$ couple lies at +0.47 V.

(18) For a discussion of this point see: (a) Goodwin, K. V.; McMillin, D. R.; Robinson, W. R. *Inorg. Chem.* **1986**, *25*, 2033 and references therein. (b) Chisholm, M. H.; Kober, E. M.; Ironmonger, D. J.; Thornton, P. *Polyhedron* **1985**, *4*, 1869.

(19) Other papers that have reported compounds of stoichiometry $TiX_2(chelate)_2$ are as follows: (a) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339. (b) Fowles, G. W. A.; Lester, T. E.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1968**, 1081.

---

# Coordination Chemistry at the Carbide Heteroatom in a Metal Cluster. Synthesis, Structure, and Bonding for $[PPN][Fe_2Co(CO)_9(CPMe_3)]$

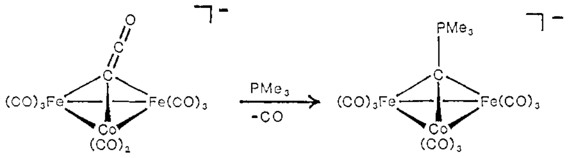
Stanton Ching, Michal Sabat, and Duward F. Shriver*

*Department of Chemistry, Northwestern University*
*Evanston, Illinois 60201*

*Received March 20, 1987*

Ligand substitution reactions at metal centers are of fundamental importance in organometallic chemistry and have numerous applications to synthesis and homogeneous catalysis.[1] Main group elements in metal clusters can support a variety of ligands, thus providing the potential for new chemistry involving ligand substitution at nonmetal sites. To date, however, facile substitution reactions of this type have been rare.[2] In the present communication, we describe unprecedented reactions in which either CO or H coordinated to carbon in a three-metal cluster are displaced by a nucleophile, trimethylphosphine.

Treatment of $[PPN][Fe_2Co(CO)_9(CCO)]$ (**1**) (PPN = bis(triphenylphosphine)iminium cation) with 1 equiv of $PMe_3$ in $CH_2Cl_2$ at room temperature generates $[PPN][Fe_2Co(CO)_9(CPMe_3)]$ (**2**) within 30 min, while liberating 1 equiv of CO, eq 1. Moderately air-stable, red–brown crystals of **2** are obtained from $CH_2Cl_2/Et_2O$/pentane in 86% yield.[3] The solution IR spectrum of **2** contains an intense $\nu_{CO}$ band at 1952 cm$^{-1}$, almost 50 cm$^{-1}$ below that of **1** and near the $\nu_{CO}$ of comparable dinegatively charged clusters.[4,5] The $^{13}C$ NMR spectrum of **2** contains a doublet centered at 203.3 ppm ($^1J_{PC} = 33.5$ Hz) assigned to the capping carbon atom. The replacement of CO by a phosphine at the carbon center of a cluster has not been previously observed, but an analogous reaction at boron has been reported for $H_3Os_3(CO)_9(BCO)$.[2] When the reaction of **1** with $PMe_3$ is monitored by NMR spectroscopy, it is found that the substitution reaction occurs by initial attack at the metal framework,[6] forming $[Fe_2Co(CO)_8(PMe_3)(CCO)]^-$. The large line width of the signal in the $^{31}P$ NMR spectrum suggests that $PMe_3$ is attached to Co. All attempts to isolate this intermediate species have failed.



1 2 (1)

The structure of **2** was determined by single-crystal X-ray diffraction,[7] Figure 1. The $\mu_3$-$CPMe_3$ ligand forms an essentially symmetric cap on the three metal atoms, and the $PMe_3$ moiety orients in a staggered conformation with respect to the triangular

---

(1) (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: 1980. (b) Parshall, G. *Homogeneous Catalysis*; Wiley-Interscience: 1980.

(2) Shore, S. G.; Jan, D.-Y.; Hsu, L.-Y.; Hsu, W. L. *J. Am. Chem. Soc.* **1983**, *105*, 5923.

(3) **2**: IR $\nu_{CO}$ ($CH_2Cl_2$) 2023 (w), 1988 (m), 1952 (s), 1901 (m) cm$^{-1}$; $^1H$ NMR ($CD_2Cl_2$, +25 °C) 1.84 (d, $^2J_{PH} = 11.9$ Hz) ppm; $^{31}P$ NMR ($CD_2Cl_2$, +25 °C) 24.6 (s) ppm; $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, –90 °C) 217.1 (s, CO), 203.3 (d, $^1J_{PC} = 33.5$ Hz, $C\text{–}P(CH_3)_3$) ppm. Anal. Calcd for $C_{49}H_{39}O_9P_3NFe_2Co$: C, 56.08; H, 3.72; P, 8.86. Found: C, 55.96; H, 3.57; P, 9.04.

(4) Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307.

(5) Ching, S.; Holt, E. M.; Kolis, J. W.; Shriver, D. F., manuscript in preparation.

(6) $[PPN][Fe_2Co(CO)_8(P(CH_3)_3)(CCO)]$: $^1H$ NMR ($CD_2Cl_2$, –90 °C) 1.37 (d, $^2J_{PH} = 8.6$ Hz) ppm; $^{31}P$ NMR ($CD_2Cl_2$, –90 °C) 2.0 (s, br) ppm; $^{13}C$ NMR ($CD_2Cl_2$, –90 °C) 216.1 (s, CO), 177.1 (d on s, $^1J_{CC} = 73.3$ Hz, $C\mathit{C}O$), 86.4 (br, $\mathit{C}CO$) ppm.

(7) Crystallographic data: $C_{49}H_{39}NO_9P_3Fe_2Co$, $M_r = 1049.4$; monoclinic, space group $P2_1/c$ (no. 14); $a = 14.370$ (3) Å, $b = 18.761$ (2) Å, $c = 17.621$ (3) Å, $\beta = 94.21$ (2)°, $V = 4738$ (2) Å$^3$; $Z = 4$, $D_{calcd} = 1.47$ g·cm$^{-3}$; $\mu$(Mo K$\alpha$) = 11.4 cm$^{-1}$. The structure was solved by direct methods in SDP (B. A. Frenz and Assoc., College Station, TX, and Enraf-Nonius, Delft, Holland, 1985) and refined by using TEXSAN 2.0 (Swepston, P. N. Molecular Structure Corporation, College Station, TX, 1986). Full-matrix least-squares refinement gave $R(F) = 0.034$ and $R_w(F) = 0.046$ for 5969 reflections with $F^2 \geq 3\sigma(F^2)$ measured up to $2\theta = 50°$ at –120 °C (Mo K$\alpha$ radiation, $\lambda = 0.71069$ Å).

0002-7863/87/1509-4722$01.50/0