Oxidatively catalyzed carbon monoxide insertion reactions with CpFeCO[P(OPh)3](.eta.1-alkenyl) complexes

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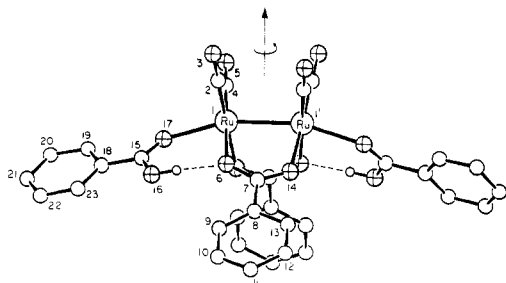
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Figure 1. Molecular structure of [Ru(PhCO$_2$)(CO)$_2$PhCO$_2$H]$_2$ (the crossed circles represent oxygen atoms). In the crystal the molecules are located on twofold rotational axes. Selected bond lengths (Å) and angles (deg) are as follows: Ru(1)–Ru(1′) = 2.637 (2), Ru(1)–C(2) = 1.826 (7), Ru(1)–C(4) = 1.842 (6), Ru(1)–O(6) = 2.146 (3), Ru(1′)–O(14) = 2.121 (4), Ru(1)–O(17) = 2.265 (5), O(6)–C(7) = 1.265 (7), C(7)–O(14) = 1.241 (8), C(15)–O(16) = 1.316 (6), C(15)–O(17) = 1.222 (8); Ru(1′)–Ru(1)–O(17) = 162.8 (1). Geometric parameters of the OH(16)⋯O(6) hydrogen bond are as follows: O(16)–H(16) = 0.90 Å, O(16)⋯O(6) = 2.605 (7) Å, H(16)⋯O(6) = 1.75 Å, and O(16)–H⋯O(6) = 158°. The acidic hydrogen H(16) was located in a difference map.

(CO)$_4$(*sec*-C$_4$H$_9$CO$_2$H) to **2**. However, we were unable to assign unambiguous molecular structure to **1** and **2**, which would conform with accepted structural rules or could be based on previously recorded examples. X-ray analyses of **1** and **2** were undertaken to solve their molecular structure (Figures 1 and 2).[8]

The unique feature of both structures is the side ligation of acid molecules. Such coordination represents, to the best of our knowledge, a new type of bonding of carboxylic acids in organometallic complexes. The specific hydrogen bonding in these systems (Figures 1 and 2) between the carboxyl and carboxylato oxygen atoms (O–O = 2.57 Å) must energetically support acid ligation. The severe distortion of the Ru octahedron in **1**, as reflected in the Ru–Ru–O(17) angle of 162.8°, is probably a consequence of the intramolecular hydrogen bonding. The acid carbonyl is essentially in the oxo form in view of its normal C=O distance (1.22, 1.25 Å). The average Ru–O distances involving the carboxylato and carboxylic acid oxygen atoms are 2.13 and 2.27 Å, respectively. Nevertheless, both **1** and **2** do not lose their acid ligands upon column chromatography (silica), indicating similar interactions in solution.

Complex **2** (Figure 2) is a centrosymmetric ruthenium tetramer that may be viewed as a dimer of two bis(*μ*-carboxylato) Ru–Ru cores, capped by two acid molecules. The dimerization involves two Ru–O bonds (2.31 Å) which, compared to the strong intracore Ru–O bonds (2.13 Å), indicate relatively tight bonding. The resulting complex is a coordinatively saturated 72-electron ruthenium tet-
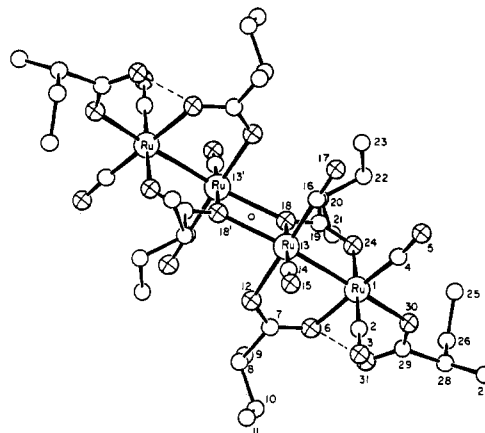
Figure 2. Molecular structure of [Ru$_2$(*sec*-C$_4$H$_9$CO$_2$)$_2$(CO)$_4$-(*sec*-C$_4$H$_9$CO$_2$H)]$_2$ (the crossed circles represent oxygen atoms). In the crystal, the molecules are located on centers of symmetry. Selected bond lengths (Å) and angles (deg) are as follows: Ru(1)–Ru(13) = 2.630 (1), Ru(1)–O(30) = 2.26 (1), Ru(1)–O(6) = 2.13 (1), Ru(1)–O(24) = 2.10 (1), Ru(13)–O(12) = 2.10 (1), Ru(13)–O(18) = 2.16 (1), Ru(1)–C(2) = 1.83 (2), Ru(1)–C(4) = 1.81 (1), Ru(13)–C(14) = 1.82 (1), Ru(13)–C(16) = 1.80 (1), C(7)–O(6) = 1.26 (1), C(7)–O(12) = 1.25 (2), C(19)–O(18) = 1.24 (2), C(19)–O(24) = 1.26 (1), C(29)–O(30) = 1.25 (2), C(29)–O(31) = 1.25 (2), O-(31)–O(6) = 2.57 (1) (hydrogen bond), Ru(13)–O(18′) = 2.314 (6) (the bridge bond; Ru(13) and O(18′) are in the two centrosymmetrically related parts of the molecule); Ru(13)–Ru(1)–O(30) = 161.7 (2), Ru(1)–Ru(13)–O(18′) = 156.5 (2). The distance between Ru(13) and Ru(13′) is 3.544 (2) Å.

ramer. In view of the similarity of the solid and solution IR spectra of **2**, it is reasonable to assume similar structure in solution.

We would like to propose that structure **2** represents a possible mode of polymerization (Scheme I) observed by Lewis et al.[2] with other acids; removal of the end acids in **2** may induce polymerization via additional Ru–O bridges. Furthermore, it is probable that the recently reported tetrameric complex[10] Ru$_4$(CO)$_8$(CH$_3$CO$_2$)$_4$(PBu$_3$)$_2$ possesses the core structure of **2**.

Supplementary Material Available: Tables of positional and thermal atomic parameters (6 pages). Ordering information is given on any current masthead page.

(8) Crystal data for [Ru(PhCO$_2$)(CO)$_2$PhCO$_2$H]$_2$, M_r = 800.7: monoclinic, space group $C2/c$ with a = 19.598 (12) Å, b = 16.909 (3) Å, c = 10.900 (6) Å, β = 118.41 (3)°; V = 3176.91 (2.91) Å^3; D_{calcd} = 1.674 g cm^{-3} for Z = 4; μ(Mo Kα) = 9.93 cm^{-1}. Full-matrix anisotropic refinement of the nonhydrogen atoms converged at R = 0.037 and R_w = 0.049 for 2087 reflections with $I \geq 3\sigma(I)$ and $2\theta < 54°$. Crystal data for [Ru$_2$(*sec*-C$_4$H$_9$CO$_2$)$_2$(CO)$_4$(*sec*-C$_4$H$_9$CO$_2$H)]$_2$, M_r = 1236.2: triclinic, space group $P\bar{1}$ with a = 9.988 (3) Å, b = 11.006 (9) Å, c = 12.916 (4) Å. α = 107.63 (4)°, β = 90.42 (3)°, γ = 109.91 (4)°; V = 1262.56 (1.28) Å^3; D_{obsd} = 1.6 g cm^{-3}, D_{calcd} = 1.556 g cm^{-3} for Z = 1; μ(Mo Kα) = 11.6 cm^{-1}. Anisotropic refinement of the core and carbonyl groups, and isotropic refinement of the partially disordered methylbutyric side chains and the acid ligand (the latter two with restrained geometry) let to R = 0.055 for 3512 reflections with $I \geq 3\sigma(I)$ and $2\theta < 54°$. Unit weights were used in this refinement. The diffraction intensities of the two compounds were measured at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.7107 Å) and employing the ω-2θ scan technique. An empirical method was used to correct the intensity data for absorption effects.[9] Both structures were solved by phase refinement and weighted Fourier techniques using the MULTAN80 system of computer programs.

(9) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* 1983, *A39*, 158.

(10) Bianchi, M.; Frediani, P.; Matteoli, U.; Menchi, G.; Piacenti, P.; Petrucci, G. *J. Organomet. Chem.* 1983, *259*, 207.

Oxidatively Catalyzed CO Insertion Reactions with CpFeCO[P(OPh)$_3$](η^1-alkenyl) Complexes

Daniel L. Reger* and **Ed Mintz**
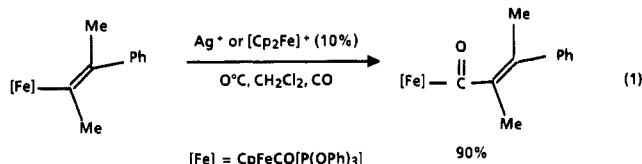*Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208*

Received July 31, 1984

Summary: Treatment of CpFeCO[P(OPh)$_3$](η^1-alkenyl) complexes with oxidizing agents such as [Cp$_2$Fe]BF$_4$ or Ce(IV) under an atmosphere of CO leads to new alkenylacyl complexes under very mild conditions.

Scheme I
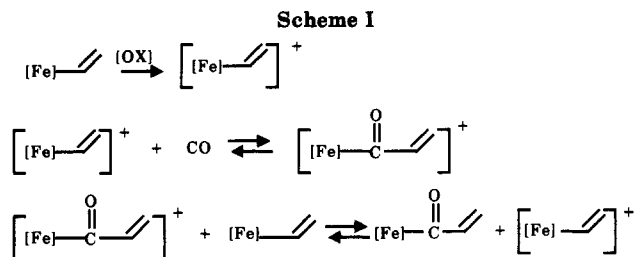
We have recently developed a variety of routes for the preparation of CpFeCO[P(OPh)$_3$](η^1-alkenyl) complexes in which there is substantial control of the substituents on the double bond in the η^1-alkenyl group.[1] For interests relating to new organometallic complexes and to the synthesis of tri- and tetrasubstituted olefins, we desired to further elaborate the alkenyl group under mild conditions by carrying out a formal CO insertion reaction leading to alkenylacyl complexes. As expected from work with similar alkyliron complexes[2] and from limited information in the literature indicating that CO insertion reactions with alkenylmetal complexes are slower than with similar alkylmetal complexes,[3] direct insertion of CO at 1 atm was unsuccessful. From the work of others, two methods to assist the reaction seemed promising. One is the addition of Lewis acids,[4] and the other is the use of catalytic amounts of oxidizing agents.[5] While the former method has not yet proven useful, we report here that reaction of these alkenyliron complexes with oxidizing agents in the presence of CO leads, under the proper conditions, to the insertion products.

Shown in eq 1 is our first successful conversion of an alkenyliron complex to an acyliron complex using catalytic amounts of either AgBF$_4$ or [Cp$_2$Fe]BF$_4$ as the oxidant.

The reaction is carried out under 1 atm of CO pressure (a balloon filled with CO gas) at 0 °C for 4 h. The isolated yield[6] (purification by column chromatography on alumina) is high. Under similar conditions, other alkenyliron

complexes did not react and were recovered in high yield (see eq 2 and 3 for two examples). For these two cases, simply lowering the reaction temperature to −78 °C causes the reactions to proceed to acyl products (eq 2 and 3). For

(3), in addition to the acyl product, ca. 30% starting material is reisolated. These reactions represent interesting cases where a reaction is successful at low temperature but only starting materials (and not other products or decomposition residues) are reisolated at a higher temperature.

Scheme I shows the overall catalytic cycle proposed (adapted to alkenyl complexes from ref 5c) for these reactions. In general, a large negative $\Delta S°$ is observed for the CO insertion step[5,7] and has been measured to be −50 ± 10 eu for the insertion reaction shown in eq 4.[5b] Pre-

$$[CpFeCO(PPh_3)(Me)]^+ + CH_3CN \rightleftharpoons$$
$$[CpFe(CH_3CN)(PPh_3)(COMe)]^+ \quad (4)$$
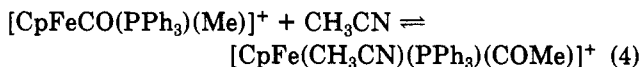
sumably lowering the temperature of reactions 2 and 3 favors the similar equilibrium step in these oxidatively catalyzed reactions leading to the preferential formation of the alkenylacyl products at low temperatures. We plan electrochemical studies of these alkenyliron and alkenylacyliron complexes to probe the system more completely.

Even at −78 °C, the alkenyl complex shown in eq 5, a
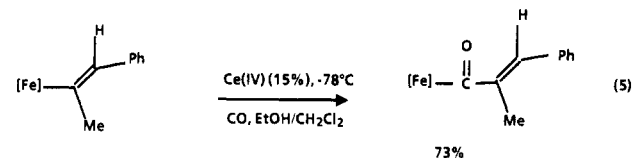
complex very similar to the one shown in eq 1, will not undergo noticeable CO insertion under these conditions. In contrast, as shown, we have found that a Ce(IV) oxidation carried out in a mixed EtOH/CH$_2$Cl$_2$ (1/2 volume ratio, EtOH is needed to solubilize the Ce(IV)) solvent system at −78 °C is successful. We are presently trying to optimize the conditions for these oxidatively catalyzed CO insertion reactions and, using a higher ratio of oxidant to iron complex, develop cleavage reactions to produce alkenyl esters.[8] In this regard, we do isolate the ester (*E*)-C(Me)(CO$_2$Et)=C(Me)Ph in 50% yield when CpFe-CO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(Me)Ph] is treated with 1 equiv of AgBF$_4$ in EtOH/CH$_2$Cl$_2$ (2/1 volume ratio).

We have also observed the oxidative catalysis of two types of isomerization reactions. As shown in eq 6,[1a] ox-

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(2) (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (b) Flood, T. C.; Campbell, K. D. *J. Am. Chem. Soc.* **1984**, *106*, 2853.
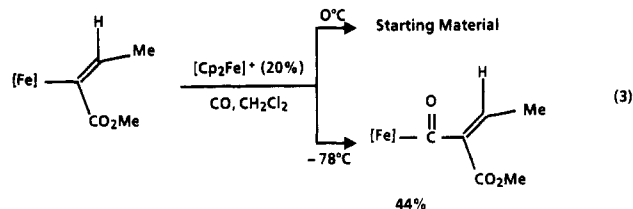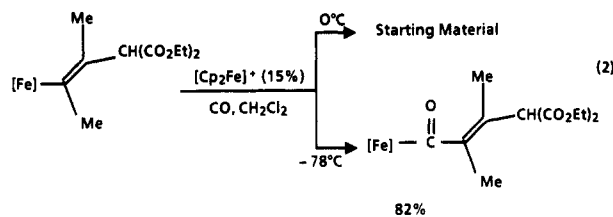
(3) (a) Baird, M. C.; Mague, J. T.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 1347. (b) Bertilo, C. A.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 228. (c) Brix, H.; Beck, W. *J. Organomet. Chem.* **1982**, *234*, 151. (d) Knifton, J. F. *J. Mol. Catal.* **1977**, *2*, 293.

(4) (a) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766. (b) Butts, S. B.; Richmond, T. G.; Shriver, D. F. *Inorg. Chem.* **1981**, *20*, 278. (c) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093. (d) Richmond, T. G.; Basolo, F.; Shriver, D. F. *Inorg. Chem.* **1982**, *21*, 1272. (e) LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312.

(5) (a) Magnuson, R. H.; Zulu, S.; T'sai, W.-M.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887–6888. (b) Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *Ibid.* **1982**, *104*, 5790–5791. (c) Magnuson, R. H.; Meirowitz, R.; Zulu, S. J.; Giering, W. P. *Organometallics* **1983**, *2*, 460–462.

(6) The new alkenylacyl complexes have been fully characterized. Most definitive are the ¹³C{¹H} NMR spectra that show resonances very similar to, but different from, the starting alkenyliron complexes and, in addition, a doublet resonance (J_{P-C} = ca. 33 Hz) at ca. 270 ppm indicative of the new acyl carbon atom: Mann, B. E.; Taylor, B. F. "¹³C NMR Data for Organometallic Compounds"; Academic Press: London, 1981.

(7) (a) Cotton, J. D.; Crisp, G. T.; Latif, L. *Inorg. Chim. Acta* **1981**, *47*, 171. (b) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946.

(8) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814.

idants catalyze a *Z–E* isomerization reaction. Similar conditions cause the double-bond isomerization reaction shown in eq 7. If these reactions are carried out in the

(6)

(7)
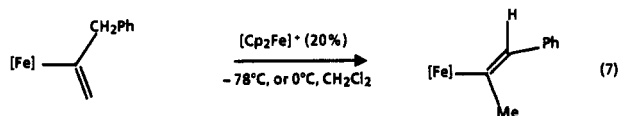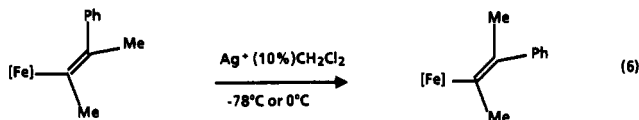
presence of CO, one does not get CO insertion of the starting materials, but the products expected when the isomerized iron complex is subjected to these conditions. Thus, for example, carrying out reaction 6 in the presence of CO yields the (*E*)-acyl product shown in eq 1. Although these are interesting isomerization reactions, they do limit the types of alkenylacyl complexes and ultimately cleaved esters that one can prepare from this methodology.

Registry No. [Fe][η¹-C(CH₂Ph)=CH₂], 92366-24-0; [Fe][η¹-(*E*)-COC(Me)=C(Me)Ph], 92366-21-7; [Fe][Nη¹-(*E*)-COC(Me)=C(Me)CH(CO₂Et)₂], 92366-22-8; [Fe][η¹-(*E*)-COC-(CO₂Me)=C(H)Me], 92366-23-9; [Fe][η¹-(*E*)-COC(Me)=C(H)Ph], 92396-62-8; [Fe][η¹-(*E*)C(Me)=C(Me)Ph], 83096-09-7; [Fe][η¹-(*E*)-C(Me)=(H)Ph], 86563-32-8; [Fe][η¹-(*E*)-C(Me)=C(Me)CH-(CO₂Et)₂], 87556-41-0; [Fe][η¹-(*E*)-C(CO₂Me)=C(H)Me], 86563-31-7; [Fe][η¹-(*Z*)-C(Me)=C(Ph)Me], 863149-30-8; [Cp₂Fe]BF₄, 1282-37-7; AgBF₄, 14104-20-2.

A Novel Synthetic Route to Cyclobutadiene Complexes of Molybdenum and Tungsten. Crystal and Molecular Structure of Mo(η-C₅H₅)(η-C₄Ph₃Me)(CO)(Cl)

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Summary: Treatment of oxocyclobutenyl complexes of molybdenum and tungsten, **1a–c**, with titanacyclobutane **2**, followed by tetrafluoroboric acid etherate, affords cationic cyclobutadiene complexes **4**, via the intermediacy of methylenecyclobutenyl compounds **3**. Reaction of cationic **4a** with chloride yields the neutral derivative **5**, which has been characterized crystallographically.

While transition-metal complexes containing cyclobutadiene ligands have aroused considerable synthetic and theoretical interest over the past two decades,³ group 6B

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(2) Alfred P. Sloan Research Fellow, 1980–1984.

complexes of this ligand are rare.⁴,⁵ Cationic group 6B derivatives are unknown,³,⁴ though some routes to cationic cyclobutadiene complexes of other transition metals have been reported.⁶ Here we describe a novel and versatile synthesis of cationic cyclobutadiene complexes of molybdenum and tungsten, from readily available precursors, and the molecular structure of a neutral molybdenum derivative.

We have reported previously the facile syntheses of oxocyclobutenyl complexes **1** from readily available cyclopropenyl cations.⁷ While the ketone functionalities of complexes **1a,b** are unreactive toward excess methylenetriphenylphosphorane (75 °C; Me₂SO),⁸ treatment with 1 equiv of the titanacycle **2**⁹ (50 °C; toluene) effects clean conversion to the methylenecyclobutenyl compounds **3a,b**.¹⁰,¹¹ Subsequent protonation with tetrafluoroboric acid in ether affords the cationic cyclobutadiene complexes **4a,b**¹² as yellow, air-stable, crystalline solids. In a similar one-pot reaction sequence, treatment of **1c** with **2**, followed by HBF₄·Et₂O, affords the permethylated cationic com-

(3) Efraty, A. *Chem. Rev.* 1977, *77*, 691–744. This provides a general review of cyclobutadiene complexes.

(4) For a recent review of group 6B organometallic compounds, see: "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3.

(5) (a) Amiet, R. G.; Reeves, P. C.; Pettit, R. *J. Chem. Soc., Chem. Commun.*, 1967, 1208. (b) Scharf, H. D.; Stahlke, K. R. *Angew. Chem., Int. Ed. Engl.* 1970, *9*, 810. (c) Davidson, J. L. *J. Chem. Soc., Chem. Commun.* 1980, 113–114. (d) Hubel, W.; Merenyi, R. *J. Organomet. Chem.* 1964, *2*, 213–221. (e) Maitlis, P. M.; Efraty, A. *Ibid.* 1965, *4*, 172–174. (f) Efraty, A.; Potenza, J. A.; Zyontz, L.; Daily, J.; Huang, M. H. A.; Toby, B. *Ibid.* 1978, *145*, 315–327. (g) Potenza, J. A.; Johnson, R. J.; Chirico, R.; Efraty, A. *Inorg. Chem.* 1977, *16*, 2354–2359. (h) Holtzapple, G. M.; Woon, P. S.; Farsona, M. F. *Inorg. Nucl. Chem. Lett.* 1976, *12*, 623. (i) King, R. B.; Efraty, A. *J. Chem. Soc., Chem. Commun.* 1970, 1370–1371. (j) Mathew, M.; Palenik, G. *Can. J. Chem.* 1969, *47*, 705–706. (k) Efraty, A. *Ibid.* 1969, *47*, 4695–4696.

(6) (a) Donaldson, W. A.; Hughes, R. P.; Davis, R. E.; Gadol, S. M. *Organometallics* 1982, *1*, 812–819. (b) Harter, P.; Pauson, P. L.; Ullah, S. S. *J. Organomet. Chem.* 1983, *247*, C27–C28. (c) Efraty, A.; Bystrek, R.; Geaman, J. A.; Sandhu, S. S.; Huang, M. H. A.; Herber, R. H. *Inorg. Chem.* 1974, *13*, 1269–1272.

(7) Hughes, R. P.; Lambert, J. M. J.; Reisch, J. W.; Smith, W. L. *Organometallics* 1982, *1*, 1403–1405. Syntheses of **1a** and **1c** are reported here; **1b** is prepared in a method analogous to that used for **1a**.

(8) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.*, 1963, *28*, 1128–1129.

(9) Titanacyclobutane **2** and its analogues have been shown to be very effective reagents for effecting the conversion of carbonyl functions into olefins. See: Buchwald, S. L.; Grubbs, R. H. *J. Am. Chem. Soc.* 1983, *105*, 5490–5491, and references cited therein.

(10) Examples of methylenecyclobutenyl complexes of Pd(II) have been reported recently: Ridgewell, P. J.; Bailey, P. M.; Wetherell, S. N.; Kelley, E. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* 1982, 999–1004.

(11) Satisfactory microanalysis results were obtained for all compounds reported. In a typical reaction **1a** (0.69 g, 1.35 mmol) was treated, under anaerobic conditions, with a solution of **2** (0.34 g, 1.23 mmol) in toluene (10 mL), and the mixture was heated at 65 °C for 4 h. The solution was cooled, and the solvent was evaporated in vacuo. The solid was extracted with hexane (2 × 30 mL) and filtered through filter aid on a Schlenk filter. Evaporation and recrystallization from hexane yielded **3a** as yellow crystals (0.56 g, 90%): IR (hexanes) ν_CO 1987, 1929 cm⁻¹; ¹H NMR (CD₃CN, shifts in ppm downfield from Me₄Si) δ 7.17–7.40 (m, 15 H, Ph), 5.20 (s, 5 H, Cp), 3.32 (s, 2 H, CH₂). Similarly prepared was **3b**: IR (hexanes) ν_CO 1983, 1921 cm⁻¹, ¹H NMR (CDCl₃) δ 6.98–7.53 (m, 15 H, Ph), 5.22 (s, 5 H, Cp), 3.28 (s, 5 H, CH₂).

(12) Typically, a solution of **3a** (0.50 g, 0.98 mmol) in ether (60 mL) was cooled to 0 °C and treated with tetrafluoroboric acid etherate (0.200 mL) to give a heavy yellow precipitate. The supernatant liquid was removed by using a cannula, and the solid was washed with ether (3 × 15 mL) and recrystallized from methylene chloride/ether to give **4a** as yellow, air-stable crystals (0.53 g, 91%): IR (CH₂Cl₂) ν_CO 2054, 2010 cm⁻¹, ¹H NMR (CDCl₃) δ 7.18–7.43 (m, 15 H, Ph), 5.65 (s, 5 H, Cp), 2.81 (s, 3 H, Me); ¹³C NMR (CDCl₃) δ 214.8 (CO), 131.6, 130.1, 129.3, 129.0, 127.8 (Ph), 97.3 (Cp), 95.4 (CPh), 89.4 (CPh), 80.8 (CMe), 13.5 (Me). Similarly prepared was **4b**: IR (CH₂Cl₂) ν_CO 2042, 1996 cm⁻¹; ¹H NMR (CDCl₃) δ 7.20–7.65 (m, 15 H, Ph), 5.84 (s, 5 H, Cp), 3.06 (s, 3 H, Me); ¹³C NMR (CDCl₃) δ 200.5 (CO), 130.9, 129.6, 129.3, 128.9, 128.7, 128.6 (Ph), 94.5 (Cp), 79.1 (CPh), 75.7 (CPh), 73.2 (CMe), 11.4 (Me). **4c:** IR (CH₂Cl₂) ν_CO 2037, 1985 cm⁻¹, ¹H NMR (CDCl₃) δ 2.17 (s, 15 H, C₅Me₅), 2.04 (s, 12 H, C₄Me₄); ¹³C NMR (CDCl₃) δ 220.2 (CO), 106.0 (*C₅*Me₅), 84.1 (*C₄*Me₄), 10.2 (C₅*Me₅*), 8.2 (C₄*Me₄*).