127.3, 146.5, 147.6, 149.1 (2-MeC_6H_4), 132.2, 135.1 (CN), 186.4 (CO). MS (EI, 70 eV): 651 (M^+, 8%), 623 ($M^+ - CO$, 7%), 559 ($M^+ - C_7H_8$).

X-ray Crystal Structure Determinations. Crystals of the three compounds were sealed under argon in thin-walled glass capillaries. All X-ray measurements were made by using an Enraf-Nonius CAD4 with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), operating in the $\omega/2\theta$ scan mode, following previously detailed procedures.[1b]

The structures were solved via application of the heavy-atom method and refined by full-matrix least-squares procedures. For structures **2** and **5a**, non-hydrogen atoms were refined with anisotropic displacement factors; hydrogen atoms were inserted in idealized positions and allowed to ride on the parent carbon atom with refined group U_{iso} values (**2**) or fixed U_{iso} values (**5a**). For structure **6**, a very strong *a*-glide pseudosymmetry (the correct space group was $P2_1/c$) caused serious correlation problems. As a result, only the Os atom was refined anistropically; all the lighter atoms were refined isotropically and no hydrogens were included. For both **5a** and **6**, severe torsional disorder in the *tert*-butyl groups also caused problems in the refinement. However, in each case it was possible to represent each Me_3C group by four atoms only. Details of the data collections and refinements are given in Table I. Atomic positional parameters are given in Tables II–IV; selected bond distances and angles in Tables V–VII.

Acknowledgment. We thank the SERC for support and Johnson Matthey PLC for loan of osmium.

Registry No. **1**, 101191-32-6; **2**, 120022-42-6; **3**, 120022-43-7; **4a**, 120022-44-8; **4b**, 120022-48-2; **5b**, 120022-49-3; **6**, 120022-46-0; Os(η^6-C_6H_6) (2-MeC_6H_4)$_2$ (PMe_3), 120022-47-1; 2,6-$Me_2C_6H_3NC$, 2769-71-3.

Supplementary Material Available: Tables of U_{ij} values and full lists of bond lengths and angles (8 pages); listings of F_o/F_c values (83 pages). Ordering information is given on any current masthead page.

Communications

Polysilyl Complexes of Platinum—Synthesis and Thermochemistry

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Received September 7, 1988

Summary: The reaction of $LiSiR(SiMe_3)_2$ (R = $SiMe_3$ or Ph) with (dcpe)$PtCl_2$ [dcpe = bis(dicyclohexylphosphino)ethane] affords two stable polysilyl derivatives of d^8 platinum, (dcpe)Pt[$SiR(SiMe_3)_2$]Cl. These compounds undergo a thermal isomerization involving a trimethylsilyl–chlorine interchange across the platinum–silicon bond. The mechanism of this isomerization is considered.

Platinum complexes have been reported to catalyze a number of polysilane-forming reactions including the dehydrogenative coupling of monomeric polyhydridosilanes[1] and the redistribution reaction of hydridodisilanes.[2] Little is known about the mechanism of these reactions; however, polysilylplatinum species seem likely candidates for chain-growing intermediates in these processes.[3] Despite their potential mechanistic significance, only one well-characterized example of a polysilylplatinum complex is known.[4,5] We therefore describe the synthesis and properties of two stable polysilyl derivatives of d^8 platinum and their novel thermal isomerizations.

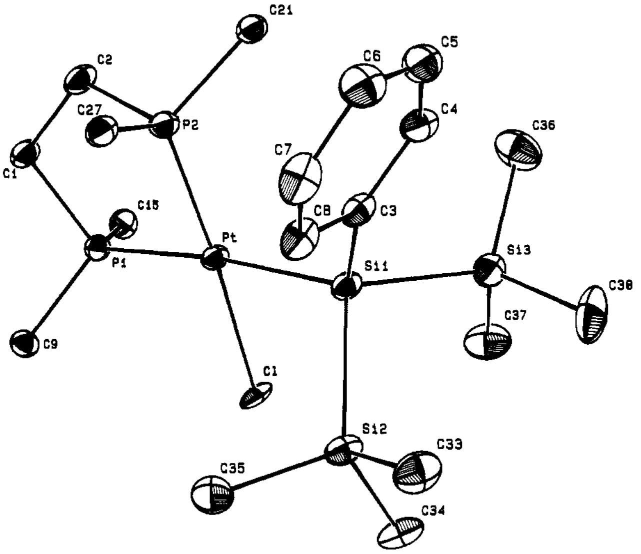

Figure 1. ORTEP diagram of (dcpe)Pt[$SiPh(SiMe_3)_2$]Cl (**1b**) showing non-hydrogen atoms. The nonpendant carbons of the cyclohexane rings have been removed for clarity. Thermal ellipsoids are at 30% probability level. Selected bond distances (Å) and angles (deg): Pt–Cl, 2.408 (1); Pt–Si1, 2.423 (2); Pt–P1, 2.326 (2); Pt–P2, 2.220 (2); Si1–Si2, 2.378 (3); Si1–Si3, 2.373 (3); Si1–C3, 1.925 (7); Cl–Pt–P1, 88.56 (6); Cl–Pt–Si1, 86.50 (6); P2–Pt–P1, 87.03 (6); P2–Pt–Si1, 97.85 (6); Si1–Si2–Si3, 105.2 (1).

Polysilylplatinum complexes **1a** and **1b** have been pre-

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(1) (a) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590–1591. (b) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068–4070.

(2) (a) Yamamoto, K.; Okimoshima, H.; Kumada, K. *J. Organomet. Chem.* **1970**, *23*, C7–C8. (b) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31–C32. (c) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C27–C30.

(3) Polysilyltitanium species have been proposed as chain-growing intermediates in the titanocene-catalyzed dehydrogenative coupling of primary silanes. Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059–4066.

(4) Lemanski, M. F.; Schram, E. P. *Inorg. Chem.* **1976**, *15*, 1489–1492.

(5) A number of stable polysilyl complexes with other transition metals are known. (a) Nicholson, B. K.; Simpson, J.; Robinson, W. T. *J. Organomet. Chem.* **1973**, *47*, 403–412. (b) Couldwell, M. C.; Simpson, J.; Robinson, W. T. *J. Organomet. Chem.* **1976**, *107*, 323–339. (c) Holtman, M. S.; Schram, E. P. *J. Organomet. Chem.* **1980**, *187*, 147–155. (d) Drahnak, T. J.; West, R.; Calabrese, J. C. *J. Organomet. Chem.* **1980**, *198*, 55–69. (e) Chisholm, M. H.; Chiu, H. T.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 4097–4102. (f) Pannel, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056–1057. (g) Roddick, D. M.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 945–946. (h) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049–2056.

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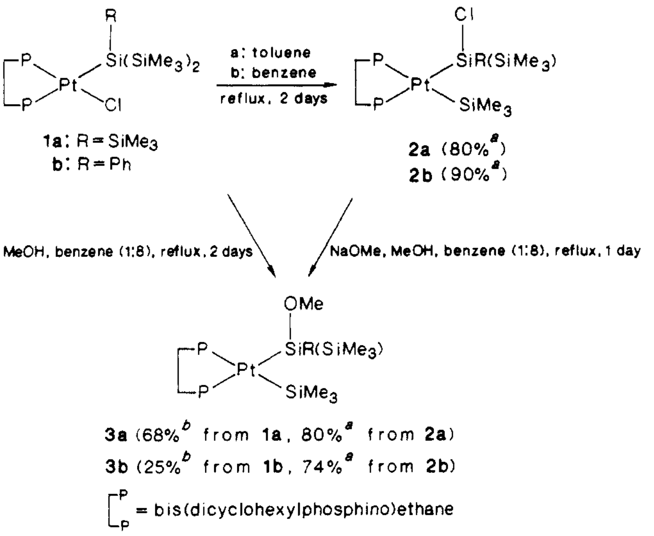
Scheme I



^{a}% yield based on ^{31}P NMR intergration. ^{b}% yield based on isolated compound.

pared by the room-temperature reaction of (dcpe)$PtCl_2$ (dcpe = bis(dicyclohexylphosphino)ethane) with $LiSiR(SiMe_3)_2$ (R = $SiMe_3$, Ph) in THF (eq 1).[6] Interestingly, only one chloride is displaced even with a large molar excess of the lithium reagent.[7]

$$(\mathrm{dcpe})\mathrm{PtCl_2} + \mathrm{LiSiR(SiMe_3)_2} \xrightarrow[\text{room temp}]{\text{THF}} (\mathrm{dcpe})\mathrm{Pt[SiR(SiMe_3)_2]Cl} + \mathrm{LiCl} \quad (1)$$

$$\mathbf{1a}\text{: R = SiMe}_3\ (58\%)$$
$$\mathbf{1b}\text{: R = Ph}\ (77\%)$$

Complexes **1a** and **1b** are white crystalline materials, inert to air and water, and soluble in most hydrocarbon solvents. An X-ray crystal structure of **1b** has been determined,[8] and the results are summarized by the ORTEP drawing in Figure 1. The coordination geometry of the platinum and metal-bound silicon are very close to idealized square planar and tetrahedral, respectively. The platinum–silicon bond length is 2.423 (2) Å; the largest value for a mononuclear complex containing a Pt–Si bond.[9]

Upon heating complexes **1a** and **1b** in refluxing aromatic solvents for 2 days, a novel isomerization occurs to give the chlorosilane derivatives **2a** and **2b**, respectively (Scheme I). These complexes may be converted in good yield to methoxysilane analogues **3a** and **3b** by reaction with NaOMe in a benzene–methanol (8:1 v/v) solution. Alternatively, the methoxysilane derivatives may be produced directly by the thermolysis of **1a** and **1b** in the same refluxing benzene–methanol (8:1 v/v) solution.[10] Presumably, the chlorosilanes **2a** and **2b** are produced as respective intermediates from the isomerization of **1a** and **1b**, which then undergo subsequent methanolysis to afford the methoxysilane products. The methoxysilane products **3a** and **3b** are remarkably stable and are purified by column chromatography.[11]

The mechanism of the isomerization of **1** to **2**[12] is of some interest since similar Si–Si bond breaking reactions must occur in the catalyzed redistribution of hydridodisilanes.[2] Our inability to trap either low-valent Pt(0)[13] or Pt(II)–silylene[14] intermediates with Et_3SiH, $EtMe_2SiCl$, or $MeOSiMe_3$ strongly suggest that the isomerization is intramolecular.

Several limiting mechanisms are envisaged that differ only in the synchronicity of group migration across the silicon–platinum bond. One possibility is the α-elimination of a trimethylsilyl group, via transition state **4**, to generate a Pt(IV)–silylene intermediate. The rearrangement is completed by the fast migration (versus intermolecular trapping) of chlorine from the platinum to the π-bound silicon. A rapid shift of chlorine to silicon may be facilitated by a bridging intermediate involving intramolecular coordination of the chlorine to the electrophilic silicon.[15] Another possibility is an initial chlorine shift from platinum to silicon, via transition state **5**, followed by fast migration of the trimethylsilyl group from silicon to platinum. Structural analogues of **5** are found in compounds containing tin–platinum–halogen triangles;[16] however, there appear to be no similar examples in silicon chemistry. A third possibility is a dyotropic mechanism involving a concerted migration of trimethylsilyl and chlorine groups across the platinum–silicon bond. The transition state for this process is depicted by **6**.

Although we are currently unable to distinguish among the three forementioned mechanisms, it is apparent that the migration of a trimethylsilyl group from silicon to platinum could be an important reaction of polysilyl-

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(6) Characterization for **1a**: ^{1}H NMR (δ, C_6D_6) 0.71 (s, $SiMe_3$), 0.98–2.62 (m, dcpe); $^{31}P\{^1H\}$ NMR (δ, C_6D_6) 65.81 (^1J(P–Pt) = 3960 Hz), 71.63 (^1J(P–Pt) = 1637 Hz); $^{29}Si\{^1H\}$ NMR (δ, CH_2Cl_2–C_6D_6 (2:1)) −91.74 ($\mathit{Si}(SiMe_3)_3$, ^1J(Si–Pt) = 878 Hz, $^2J(Si\text{–}P_{cis})$ = 11 Hz, $^2J(Si\text{–}P_{trans})$ = 165 Hz), −9.68 (s, $Si(\mathit{Si}Me_3)_3$). Anal. Calcd for $C_{35}H_{75}ClP_2PtSi_4$: C, 46.67; H, 8.39; Si, 12.47. Found: C, 45.34; H, 8.25; Si, 12.55. Characterization for **1b**: ^{1}H NMR (δ, CD_2Cl_2) 0.25 (s, $SiMe_3$), 0.9–2.58 (m, dcpe), 7.0–7.68 (m, Ph); $^{31}P\{^1H\}$ NMR (δ, C_6D_6) 59.50 (^1J(P–Pt) = 3992 Hz), 71.60 (^1J(P–Pt) = 1508 Hz); $^{29}Si\{^1H\}$ NMR (δ, CH_2Cl_2–C_6D_6 (2:1)) −34.46 ($\mathit{Si}Ph(SiMe_3)_2$, ^1J(Si–Pt) = 851 Hz, $^2J(Si\text{–}P_{cis})$ = 7 Hz, $^2J(Si\text{–}P_{trans})$ = 168 Hz), −9.70 (s, $SiPh(\mathit{Si}Me_3)_2$). Anal. Calcd for $C_{38}H_{71}ClP_2PtSi_3$: C, 50.45; H, 7.91; Si, 9.31. Found: C, 49.46; H, 7.90; Si, 9.69.

(7) The exclusive formation of monosubstituted complexes may be attributed to the steric bulk of the silyllithium reagent. A similar observation is noted for the reaction of (dcpe)$PtCl_2$ with organolithium reagents and Grignards. Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436–1448.

(8) Crystal data: dimensions, 0.46 × 0.41 × 0.40 mm; crystal system, monoclinic; space group, $P2_1/n$; a = 12.761 (4) Å, b = 17.940 (3) Å, c = 20.194 (3) Å, β = 107.29 (2)°; Z = 4; absorption coefficient = 34.41 cm^{-1}; Mo Kα radiation with graphite monochromator, 2θ scan range = 1.0–44°; 5405 unique reflections with $3988 \geq 3\sigma(I)$. Structure solution was obtained by direct methods and refined to convergence with full-matrix least squares; R = 3.1, R_w = 4.3.

(9) Aylett, B. J. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 1–33.

(10) The major competing reaction form the thermolysis of **1b** in MeOH/benzene mixtures is loss of HCl and orthometalation of the phenyl ring (75% yield). However, the methoxysilane complex **3b** is formed in reasonable yield (25%), and no other products are observed.

(11) The spectroscopic data are totally consistent with the proposed structures for complexes **2a**, **2b**, **3a**, and **3b**. The combustion analysis for these complexes, however, give erroneous values due to the metal-catalyzed formation of β-SiC.[5g] The usual result is a variable but low value for carbon. The variance in our combustion results are consistent with previously reported cases.

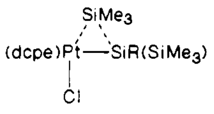
(12) A similar trimethylsilyl–chlorine interchange across a phosphorus–silicon bond has been reported: Cowley, A.; Newman, T. H. *Organometallics* **1982**, *1*, 1412–1413.

(13) The possibility of reductive elimination of $ClSiR(SiMe_3)_2$ to give (dcpe)Pt, followed by reinsertion of (dcpe)Pt into the Si-Si bond of the chlorosilane was considered. However, the highly reactive (dcpe)Pt is known to readily insert into the C-H bonds of aromatic solvents to afford stable complexes. No such complexes were observed in our experiments. Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1149–1162.

(14) The 1,2 elimination of Me_3SiCl to give (dcpe)Pt=$SiR(SiMe_3)$ followed by readdition of the chlorosilane to the silylene complex in the opposite sense provides another pathway to isomerization. The absence of trapping products, especially with $EtMe_2SiCl$, mitigates against this possibility.

(15) Examples of intermolecular coordination to silicon are found in stable base adducts of metal–silylene complexes. (a) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. L. *J. Am. Chem. Soc.* **1987**, *109*, 5872–5873. (b) Zybill, C.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 669–670. (c) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092–4093.

(16) van der Zeijden, A. A. H.; van Koten, G.; Wouters, J. M. A.; Wijsmuller, W. F. A.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 5354–5361.



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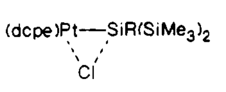

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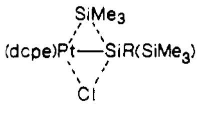

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platinum compounds. These results are consistent with the proposal that α-silyl elimination and the formation of silyl(silylene) complexes occur early in the catalytic redistribution of hydridodisilanes by platinum complexes.[2b-c,17] Further experiments along these lines are in progress.

Acknowledgment. We wish to thank the donors of the Petroleum Research Foundation, administered by the American Chemical Society, and the Louisiana Board of Regents for support of this work.

Supplementary Material Available: Spectroscopic characterizations of new compounds and complete tables of positional parameters, bond lengths and angles, and least-squares planes for **1b** (21 pages); a listing of structure factors for **1b** (40 pages). Ordering information is given on any current masthead page.

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(17) (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263-9264. (b) Ojima, I.; Inaba, S. I.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7-C8.

A Novel Synthesis of Functional, Cyclic (Trimethylenemethane)tricarbonyliron Complexes by the Reactions of α-Substituted Allenyllithium Reagents with Pentacarbonyliron

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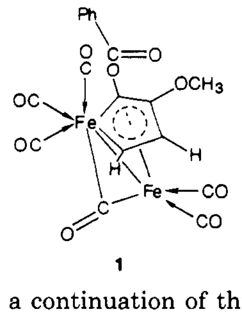
Summary: The reaction of (α-methoxyallenyl)lithium with pentacarbonyliron at −78 °C, followed by addition of an acid chloride, gives organoiron products in which the organic ligand is composed of a four-membered ring, three carbon atoms of which plus an exo =CH_2 group make up a trimethylenemethane unit which is bonded to an $Fe(CO)_3$ moiety, $[\eta^4\text{-RC(O)OC}\overline{\text{C(=CH}_2\text{)C(OMe)C}}\text{=O]Fe(CO)}_3$. The allenyllithium reagents CH_2=C=C(SMe)Li and CH_2=C=C(NMe_2)Li form similar products in their reactions with $Fe(CO)_5$.

In earlier work, we found the reaction of (α-methoxyallenyl)lithium with $Fe_3(CO)_{12}$, followed by addition of benzoyl chloride, to give as an unexpected product, the ferrole 1, whose structure was established by X-ray crystallography.[1] In a continuation of this study, we have investigated the reaction of (α-methoxyallenyl)lithium with $Fe(CO)_5$.



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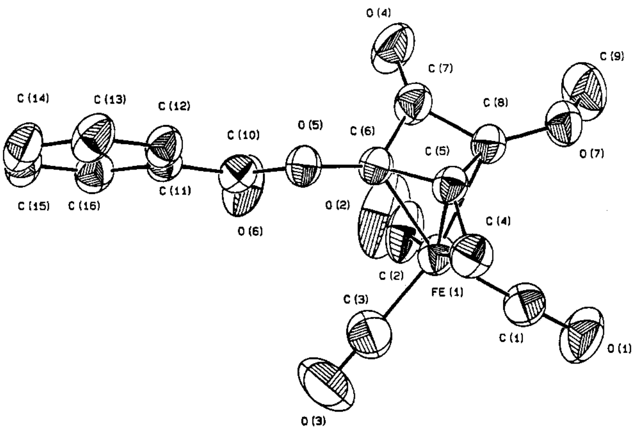

Figure 1. ORTEP representation of compound **2a** (40.0% probability ellipsoids). Hydrogen atoms are omitted for clarity. Important bond distances (Å): Fe-C(3), 1.785 (6); Fe-C(1), 1.785 (5); Fe-C(2), 1.792 (6); Fe-C(5), 1.944 (4); Fe-C(6), 2.068 (4); Fe-C(8), 2.128 (4); Fe-C(4), 2.208 (4); O(5)-C(6), 1.382 (5); O(4)-C(7), 1.202 (5); O(7)-C(9), 1.416 (6); C(4)-C(5), 1.388 (6); O(1)-C(1), 1.146 (5); O(2)-C(2), 1.134 (6); O(3)-C(3), 1.137 (6); C(6)-C(7), 1.493 (6); C(7)-C(8), 1.497 (6); O(7)-C(8), 1.337 (5). Important bond angles (deg): C(6)-C(7)-C(8), 85.1 (4); C(5)-C(8)-C(7), 90.4 (4); C(8)-C(5)-C(6), 89.8 (4); C(5)-C(6)-C(7), 90.5 (4); C(4)-C(5)-C(6), 127.0 (4); C(4)-C(5)-C(8), 128.7 (4).

The CH_2=C=C(OMe)Li reagent was prepared[2] by the reaction of methoxyallene[3] with an equimolar quantity of *n*-butyllithium in THF at −78 °C (all operations under nitrogen). In a typical experiment, a 100-mL flask with a side arm, equipped with a stir bar and a rubber septum, was charged with 15 mL of dry THF and 5.00 mmol of $Fe(CO)_5$. The solution was cooled to −78 °C, and then 5.40 mmol of (α-methoxyallenyl)lithium in 5 mL of THF, also at −78 °C, was cannulated into the $Fe(CO)_5$ solution. The resulting mixture was stirred for 1 h at −78 °C, during which time a color change from light orange to orange-red was noted. After the mixture had been allowed to warm to room temperature (giving a dark red solution), it was stirred for 1 h more and then 5.40 mmol of benzoyl chloride was added. The reaction mixture was stirred at room temperature for some hours, and then the solvent was removed at reduced pressure. The residual red oil was passed through a thin pad of silicic acid (elution with 8:1 dichloromethane/pentane). The product was isolated from the eluate by preparative TLC (silica gel, 1:1 v/v dichloromethane/pentane) as air-stable, yellow crystals, mp 93–94 °C (0.74 g, 43% yield). A similar reaction, carried out with a slow stream of carbon monoxide bubbling through the reaction mixture until such time as the benzoyl chloride was added, gave this product in 68% yield. On the basis of its analysis, EI mass spectrum, and ^1H and ^{13}C NMR spectra[4] the product was identified as **2a**, a (tri-

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(1) Seyferth, D.; Archer, C. M.; Dewan, J. C. *J. Organomet. Chem.* **1986**, *308*, C5.

(2) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*, 1st ed.; Elsevier: Amsterdam, 1981, p 92.

(3) Reference 2, p 23.

(4) Anal. Calcd for $C_{16}H_{10}O_7Fe$: C, 51.92; H, 2.73. Found: C, 51.85; H, 2.77. EI mass spectrum: inter alia, M^+ and $M^+ - n$CO (n = 1–4) fragment ions. IR (CCl_4, cm^{-1}): ν(C=O), 1780, 1755, 1745; terminal C≡O, 2085 (vs), 2005 (vs), 2000 (vs). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.81 (s, 3 H, OCH_3), 4.22 (d, $^2J_{gem}$ = 2.39 Hz, 1 H, =CH_2), 4.43 (d, $^2J_{gem}$ = 1.52 Hz, 1 H, =CH_2), 7.43 (t, J = 7.82 Hz, 2 H, Ph), 7.59 (t, J = 7.43 Hz, 1 H, Ph), 7.99 (d, J = 8.28 Hz, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ_C 60.40 (q, J = 146.3 Hz, OCH_3, 69.48 (t, J = 166.5 Hz, =CH_2), 94.09 (s, *C*OC(O)Ph), 108.77 (s, *C*=CH_2), 123.90 (s, *C*OCH_3), 127.50 (s, ipso Ph), 128.54 (d, J = 153.1 Hz, Ph), 130.03 (d, J = 166.5 Hz, Ph), 133.98 (d, J = 157.1 Hz, Ph), 163.12 (s, CO*C*(O)Ph), 170.15 (s, CH_3OC*C*=O), 205.43, 206.25, 208.90 (all s, Fe—CO).