difficulty was overcome by using an excess of reagents and running the reaction under strict control. To a solution of ketone **1a** in benzene was added an excess of $BF_3 \cdot OEt_2$ (ca. 10 equiv to the substrate). The resulting dark violet solution was stirred for 30 min under a nitrogen atmosphere, and a large excess of diazomethane in ether, free from alcohols and moisture, was added to the solution of the aged complex. Chromatographic separation of the product yielded bridge-enlarged α-oxoferrocenophane **2a** (18%) as orange-yellow crystals: mp >300 °C; IR, 1655 cm^{-1} ($\nu_{C=O}$); high-resolution MS, *m/z* 470.2293 (calcd mol wt, 470.2270); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 24.2–44.3 (11 peaks, methylene C), 80.5–85.7 (six peaks, Cp C), 209.31 (C=O); absorption spectrum λ_{max} (THF), 425 nm (ϵ 313). Reduction of the ketone **2a** with $LiAlH_4/AlCl_3$ in ether quantitatively gave the target compound **2a**, as yellow needles: mp >300 °C; high-resolution MS, *m/z* 456.2470 (calcd mol wt, 456.2477); absorption spectrum λ_{max} (THF), 403 nm (ϵ 89). The ^1H NMR spectrum (400 MHz, $CDCl_3$) of **2b** showed two signals for the methylene resonances (δ 1.97, $W_{h/2}$ = 24.8 Hz, α-CH_2; δ 2.54, $W_{h/2}$ = 15.2 Hz, β-CH_2).[19] No other signal was present. The $^{13}C\{^1H\}$ NMR spectrum (25.1 MHz, $CDCl_3$), obtained under complete decoupling conditions, was dramatically simple as expected. Only three signals were observed at δ 84.46, 26.90, and 23.55, and these were assigned to the Cp rings and the β- and α-methylene carbons, respectively.[19] The NMR spectra thus indicate that the compound has D_{5d} or D_{5h} symmetric structure.

The crystal structure of **2b** was determined by X-ray diffraction.[20] Figure 1a,b shows the molecular structure in which each atom is drawn by a thermal ellipsoid of 30% probability. Whereas the thermal vibrations of the atoms of the ferrocene nucleus are small and almost isotropic, those of the β- and β'-carbon atoms on the bridges are large and remarkably anisotropic, their major axes being directed almost perpendicular to the C_β–$C_{\beta'}$ bonds. The distances between the β- and β'-carbons are unusually short (1.286 (17)–1.356 (13) Å), which may result from the anisotropic thermal motions and/or static disorders of the bridging carbons in the crystal. In fact, if one calculates the C_β–$C_{\beta'}$ distances by taking the positions of the C_β and $C_{\beta'}$ atoms, not at the center of the ellipsoid but shifted in the opposite direction to each other within their thermal ellipsoids, one can find the positions that give a normal C–C bond length. The Cp rings show a good planarity and the deviations of the Cp carbon atoms from their own least-squares planes are small (below 0.006 Å). On the other hand, all the α-carbon atoms linked to the Cp ring deviate by 0.127 (6)–0.160 (5) Å from this plane in the opposite direction to the iron atom. The Cp rings are almost stacked parallel to each other and are in an eclipsed conformation about the Cp–Fe–Cp axis. The distance between the Cp ring and iron atom is 1.622 (3) Å, which is slightly smaller than that found in the corresponding tetrabridged ferrocenophane (1.630 (2) Å).[21] The whole shape of the superferrocenophane[22] is nearly spherical as shown in Figure 1c.

Supplementary Material Available: Tables of atomic coordinates, temperature factors, bond lengths and angles, and deviations of atoms from the least-squares plane through the Cp ring (8 pages). Ordering information is given on any current masthead page.

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(18) Hisatome, M.; Kawajiri, Y.; Yamakawa, K. *J. Organomet. Chem.* **1982**, *226*, 71.

(19) The assignment of the proton and carbon signals was made by measurements of selective $^{13}C\{^1H\}$ decoupling and nondecoupling ^{13}C NMR spectra.

(20) Crystals grown from a 1,2-dichloroethane solution were transparent yellow thick plates. A small specimen with approximate dimensions 0.2 × 0.3 × 0.5 mm was cut from the crystal and used for the X-ray diffraction study. The lattice constants and intensity data were measured on a Phillips PW-1100 diffractometer using graphite monochromated Mo Kα radiation. Crystal data: $C_{30}H_{40}Fe$, MW = 456.5, tetragonal, space group $I\bar{4}2d$, a = 15.453 (8) Å, c = 18.968 (10) Å, V = 4529 Å^3; Z = 8, D_{calcd} = 1.334 g cm^{-3}, μ for Mo Kα = 6.79 cm^{-1}. Intensities of 2603 reflections were measured as above the $2\sigma(I)$ level out of 3193 within the 2θ range of 6–60° (involved in an octant of the reciprocal space). These data were processed to yield 1279 independent structure factors by averaging symmetry-equivalent reflections (*khl* vs. *hkl*) and by correcting for Lorentz and polarization factors. No correction for absorption was.applied. The crystal structure was determined by the heavy-atom method and refined to an *R* factor of 0.065 by the block-diagonal matrix least-squares calculations. In the final stage of the refinement, the anomalous dispersion corrections were applied for iron atoms. (The space group, $I\bar{4}2d$ has a glide plane and nonenantiomorphic but has no center of symmetry.) Hydrogen atoms were not included. If the hydrogen atoms were placed at the calculated positions and refined with isotropic temperature factors, the *R* factor decreases to 0.053, but in view of the fact that the bridging carbon atoms have a pronounced temperature factor, all the hydrogen atoms are not shown in Figure 1.

(21) Kawajiri, Y. Ph.D. Thesis, Science University of Tokyo, Tokyo, 1982.

(22) The central metal ion of the superferrocenophane is bound to the two aromatic π-electron systems. Complete hydrogenation of the Cp rings may liberate a neutral iron atom from the bond. If the iron atom escapes from the molecule through small openings between the methylene chain, a cage hydrocarbon will be formed. If not, a novel cage compound keeping the neutral iron atom inside the hydrocarbon network will be generated from the superferrocenophane. Further experiments for testing these interesting questions are in progress.

New Methods for the Generation of Episulfonium Ions. An Application to the Synthesis of Carbocycles via Sulfenium Ion Promoted Arene–Alkene Cyclizations

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Received September 9, 1985

New synthetic operations which result in the annulation of carbocyclic derivatives with the *net incorporation* of latent functionality will exhibit great utility for the elaboration of natural products. In principle, the intramolecular interception of a highly reactive episulfonium ion by an appropriate carbon-centered nucleophile would constitute a powerful method for effecting cyclizations of this type. In this communication we report a novel and exceptionally versatile protocol for the generation of sulfenium ion equivalents and delineate the *first examples of cationic arene–alkene cyclizations* mediated by these species (Scheme I).

All of the previously reported procedures for the carbofunctionalization of alkenes via episulfonium ions require the use of sensitive silver salts[1–3] or result in the formation of the nucleophilic byproduct dimethyl sulfide.[4–6] These characteristics have imposed severe limitations on the application of episulfonium ion initiated cyclizations to carbocycle annulation. We have found that representative annulations of this type proceed efficiently in the presence of methyl benzenesulfenate (**4**)[7] and an appropriate Lewis acid.[8] Accordingly, exposure of the substrate **5a**[11] to 1.05 equiv

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(1) Smit, W. A.; Krimer, M. Z.; Vorobeva, E. A. *Tetrahedron Lett.* **1975**, 2451.

(2) Smit, W. A.; Semenovski, A. V.; Kucherov, V. F.; Chernova, T. N.; Krimer, M. Z.; Lubinskaya, O. V. *Tetrahedron Lett.*, **1971**, 3101.

(3) Smit, W. A.; Zetirov, N. S.; Bodrikov, I. V.; Krimer, M. Z., *Acc. Chem. Res.* **1979**, *12*, 282. Alderdice, M.; Weiler, L. *Can. J. Chem.* **1981**, *59*, 2239.

(4) Trost, B. M.; Martin, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 4263.

(5) Trost, B. M.; Shibata, T.; Martin, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 3228.

(6) Trost, B. M.; Shibata, T. *J. Am. Chem. Soc.* **1982**, *104*, 3225.

(7) Methyl benzenesulfenate can be conveniently prepared on a *molar* scale in 90% yield via the treatment of phenylsulfenyl chloride with methanol in the presence of triethylamine: Chang, L. L.; Denney, D. B.; Denney, D. Z.; Kazior, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 2293.

(8) Precedent for "sulfenate activation" rests in the documented proclivity of methyl benzenesulfenate to undergo exchange reactions with (trimethylsilyl)amines,[9] cyanide,[10] and chloride.[10]

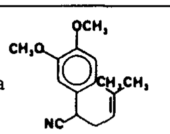
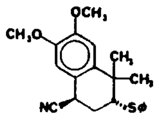
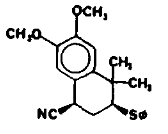
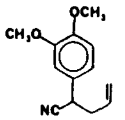
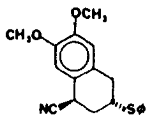
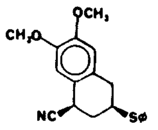
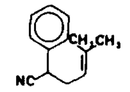
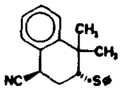
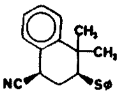
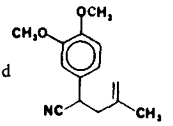
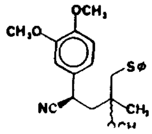
(9) Armitage, D. A.; Clark, M. J.; Kisey, A. C. *J. Chem. Soc. C* **1971**, 3867.

(10) Harpp, D. N.; Friedlander, B. T.; Larsen, C.; Steliou, K.; Stockton, A. *J. Org. Chem.* **1978**, *43*, 3481.

(11) The substrates **5a–d** were conveniently prepared via the sequential treatment of (3,4-dimethoxyphenyl)acetonitrile with 1 equiv of LDA followed by 1 equiv of the appropriate allylic halide. All new compounds exhibited satisfactory NMR, and IR spectra as well as elemental (C, H) analyses or exact mass.

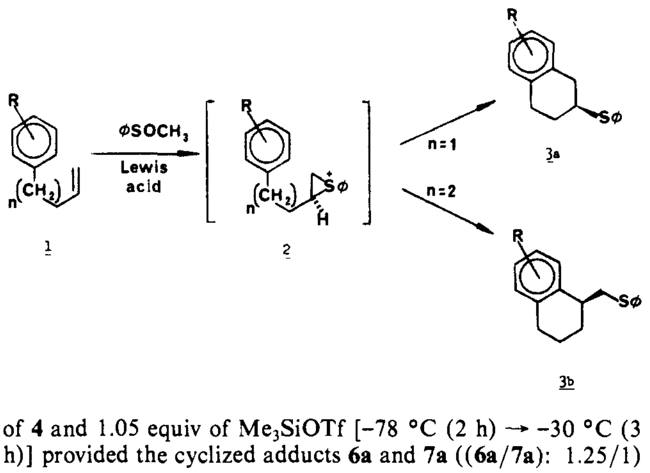
0002-7863/86/1508-1334\$01.50/0

Table I. Carbocycle Annulations Mediated by $PhSOCH_3$ and Lewis Acids[15]

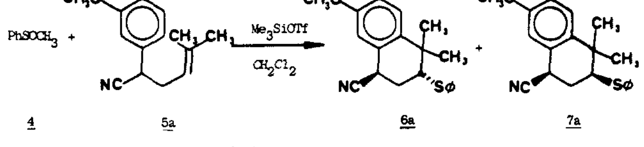
substrate[a]	Lewis acid[b,c]	conditions, °C, *t*	products[d]	ratio, yield[e,f]	
5a 	TMSOTf (1 equiv) BF_3 (2 equiv)	-78, 2 h; -30, 3 h -78, 2 h; -30, 3 h	 6a  7a	1.25:1 1.05:1	97% 96.5%
5b 	TMSOTf (1 equiv) BF_3 (2 equiv)	-78, 2 h; -35, 2 h; -20, 12 h -78, 2 h; -35, 2 h; -20, 12 h	 6b  7b	1.45:1 1.30:1	31% 68%
5c 	BF_3 (2 equiv)	-78, 1 h; -40, 1 h; -20, 12 h	 6c  7c	1:1.50	47%
5d 	TMSOTf (1 equiv)	-78, 2 h; -20, 10 h	 8		35%

[a] In all instances a 1.05:1 ratio of $PhSOCH_3$ (**4**) to the substrate was employed. [b] The use of 2 equiv of BF_3 (as a stock solution in CH_3NO_2) provided the optimum yields of cyclized products. [c] Boron trifluoride ether complex was less effective than CH_3NO_2 solutions of BF_3 for promoting cyclizations. [d] No products arising from the ortho mode of cyclization were observed. [e] All yields correspond to chromatographically purified products. [f] All compounds were fully characterized by 300-MHz NMR and IR spectroscopy and possessed satisfactory elemental (C, H) analyses. [g] In this instance simple addition of $PhSOCH_3$ to the pendant alkene occurred to the exclusion of cyclization.

Scheme I



of **4** and 1.05 equiv of Me_3SiOTf [-78 °C (2 h) → -30 °C (3 h)] provided the cyclized adducts **6a** and **7a** ((**6a**/**7a**): 1.25/1)



in 97% isolated yield.[12,13] A more revealing indication of the generality associated with this method was provided by the treatment of the substrates **5b–d** with methyl benzenesulfenate (**4**) in the presence of Lewis acids. The results of this study are compiled in Table I.[15]

It is evident that methyl benzenesulfenate (**4**) in combination with BF_3 or Me_3SiOTf constitute effective binary systems for promoting cationic arene–alkene cyclizations in a wide range of substrates. It is significant that both activated and *nonactivated* aromatic nuclei (e.g., **5c**) participate in these cyclizations with reasonable to high efficiency. It is noteworthy, but not particularly surprising, that the "anti-Markovnikov" adducts **6b** and **7b** were formed as the exclusive products via the cyclization of **5b**. The colinear trajectory required for the alternative "Markovnikov" mode of ring closure is unattainable in the episulfonium ions derived from **5b**. The highly electrophilic $PhSOCH_3$–$2BF_3$ combination is capable of initiating cyclizations involving either mono- or trisubstituted alkenes (e.g., **5a** or **5b**). By way of contrast, the more *selective* $PhSOCH_3$–Me_3SiOTf binary system is sufficient for promoting annulations involving trisubstituted alkenes.[16]

Episulfonium ions have been shown to undergo nucleophilic scission with net inversion of configuration.[3] An investigation designed to reveal the stereochemistry of cyclization was conducted in the following manner. Addition of (*E*)-1-(3,4-methylenedi-

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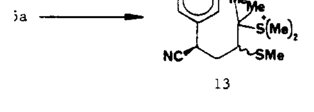
(12) It is significant that an attempt to effect the cyclization of **5a** by using dimethyl(methylthio)sulfonium tetrafluoroborate (DMTSF)[4–6] afforded only the simple addition product **13**. This result is a direct consequence of the nucleophilic byproduct $(CH_3)_2S$ being formed when DMTSF is used as a sulfenylating agent.



13

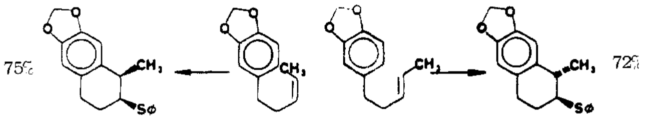
(13) Analogous cyclizations of the substrates **5a** and **5b** using phenylsulfenyl chloride in conjunction with silver tetrafluoroborate[1,2] or silver triflate were also achievable albeit in low yield.[14] Silver ion mediated carbocycle annulations were inferior to the present method in all cases examined.[14]

(14) Edstrom, E. D.; Livinghouse, T. *J. Chem. Soc., Chem. Commun.*, in press.

(15) In a representative cyclization, 1.05 equiv of $PhSOCH_3$ was treated with 2 equiv of BF_3 (as a stock solution in CH_3NO_2) in CH_2Cl_2 at -78 °C. A solution of the substrate (1 equiv) in CH_2Cl_2 was then added at -78 °C. The resultant solution was then stirred at -78 °C for 2 h and -35 °C for 2 h and stored at -20 °C for 10 h. The reaction mixture was then quenched with 10% aqueous $NaHCO_3$ and processed.

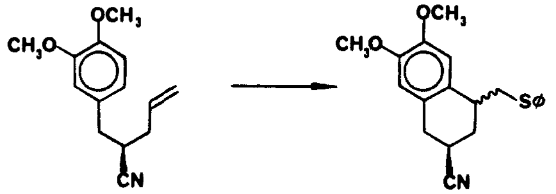
(16) The utility of the $PhSOCH_3$–Me_3SiOTf binary system for promoting chemoselective polyene cyclizations initiated by trisubstituted alkenes is currently under investigation. An analogous example involving a triene cyclization mediated by mercuric trifluoroacetate has recently appeared: McMurry, J. E.; Erion, M. D. *J. Am. Chem. Soc.* **1985**, *107*, 2712.

oxyphenyl)-3-pentene **9a** to a solution of PhSOCH$_3$ (1.05 equiv) and BF$_3$ (2.1 equiv, 0.8 M in CH$_3$NO$_2$) in CH$_2$Cl$_2$ [-78 °C (2 h) $\rightarrow$ -40 °C (2 h)] afforded the *trans*-tetralin derivative **10a** as the exclusive product in 75% chromatographed yield.[17] In complete accord with this observation the cyclization of the corresponding *Z* isomer **9b** gave only the cis adduct **10b** in 72% isolated yield.[17] These results are consistent with the existance of bridged episulfonium ions as transient intermediates in the preceeding reactions.

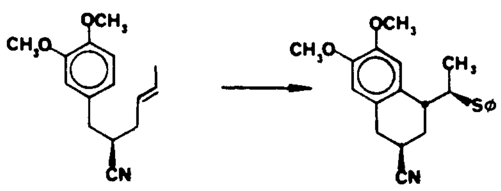


10b 9b 9a 10a

A study to determine the exo/endo mode selectivity of cyclization (leading to six- or seven-membered rings, respectively) was carried out as follows. Exposure of the 2-(2-phenylethyl)pentenenitrile **11a** to PhSOCH$_3$ (1.05 equiv) and BF$_3$ (2.10 equiv, 0.8 M in CH$_3$NO$_2$) in CH$_2$Cl$_2$ [-78 °C (2 h) $\rightarrow$ -30 °C (10 h)] furnished the cyclized adducts **12a,b** (12b/12c: 1/1) in 52% purified yield. Similarly, sulfenylative cyclization of **11b** [PhSOCH$_3$ (1.05 equiv), SnCl$_4$ (1.00 equiv), -78 °C (2 h) $\rightarrow$ -30 °C (10 h)] provided the tetralin derivative **12c** as the major diastereomer in 51% recrystallized yield.[18] In neither instance were products possessing seven-membered rings isolated.



11a 12a,b



11b 12c

The synthetic viability of sulfenium ion promoted carbocycle annulations reliant upon methyl benzenesulfenate–Lewis acid binary systems has been firmly established. Studies on the utility of this methodology for effecting polyene cyclizations as well as the development of a related procedure for the generation of episelenonium ions are currently under way. The application of these new methods for cationic annulation to the construction of naturally occurring ring systems will be described in future reports from these laboratories.

Acknowledgment. Support for this research by a grant from the National Institutes of Health (GM-32000) is gratefully acknowledged. This paper is dedicated to the memory of Professor Robert V. Stevens.

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[17] Support for these stereochemical assignments was provided by 300-MHz NMR. Specifically, the quasi-equatorial methyl substituent of the trans derivative **10a** was deshielded (δ 1.38, d, J = 7.0 Hz) relative to the quasi-axial methyl (δ 1.29, d, J = 7.0 Hz) of the *cis*-tetralin **10b**. In consonance with this observation, the quasi-equatorial benzylic methine of cis **10b** was deshielded (δ 3.03) relative to its quasi-axial counterpart (δ 2.92) in trans **10a**.

[18] The stereochemistry of **12c** has been tentatively assigned on the basis of 300-MHz ^{1}H NMR spectral data. A definitive stereochemical assignment awaits single-crystal X-ray structure determination.

(Hydroxyacetyl)iridium and -rhodium Complexes: Model Compounds for CO Hydrogenation

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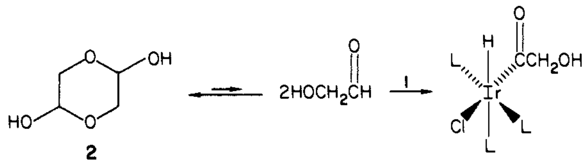
Contribution No. 3910, Central Research & Development Department, E. I. du Pont de Nemours & Co. Experimental Station, Wilmington, Delaware 19898

Received November 5, 1985

Hydroxyacetyl complexes are postulated as intermediates in the direct conversion of synthesis gas to oxygenated products[1] and in the hydroformylation of formaldehyde to glycolaldehyde, an ethylene glycol precursor[2] (Scheme I).

Whereas various hydroxymethyl complexes are now known, Fe(COCH$_2$OH)[P(OMe)$_3$]$_2$(CO)Cl[3] obtained as an isomeric mixture is the only hydroxyacetyl complex reported and no (hydroxyacetyl)metal hydrides are known. A chelate-stabilized hydroxyacyl complex has been reported very recently.[4] The lack of hydroxyacetyl complexes is perhaps due in part to difficulties in carbonylation of hydroxymethyl complexes.[5,6] We report here the synthesis of such complexes by oxidative addition reactions of 2,5-dihydroxy-1,4-dioxane (glycol aldehyde dimer) to Ir(I) and Rh(I) complexes, the reversal of the postulated product-forming step in formaldehyde hydroformylation. The thermally induced elimination modes of the rhodium complexes bear directly on the steps postulated in Scheme I.

Stirring a suspension containing equivalent amounts of (C$_8$H$_{14}$)Ir(PMe$_3$)$_3$Cl (**1**) (C$_8$H$_{14}$ = cyclooctene) and 2,5-dihydroxy-1,4-dioxane (**2**) in toluene for 16 h under N$_2$, filtration, and evaporation of the solvent yield a yellow oil. Extraction of the oil with pentane and evaporation of the solvent yields the pure complex **3** as a light yellow solid in 60% yield (eq 1). The structure of **3** is unambiguously assigned on the basis of ^{1}H NMR, ^{31}P NMR, and IR[7] and is confirmed by a single-crystal X-ray diffraction study (Figure 1).[8,9]



(1)

2

3, L=PMe$_3$

Complex **3** crystallizes in a $P\bar{1}$ space group with two molecules per asymmetric unit, for a total of four molecules per unit cell. Coordination about the iridium is octahedral with the expected distortion arising from the lack of steric bulk of the hydride ligand. The Ir–P trans to the hydride is 0.05 Å longer than the Ir–P bond

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[1] (a) Rathke, J. W.; Feder, H. M. "Catalysis of Organic Reactions"; Moser, W. R., Ed.; Marcell Dekker: New York, 1981; p 219. (b) Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136. (c) Dombek, B. D. *Adv. Catal.* **1983**, *32*, 325.

[2] (a) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *172*, C27. (b) Spencer, A. *Ibid.* **1980**, *194*, 113. (c) Chan, A. S. C.; Carroll, W. E.; Willis, W. E. *J. Mol. Catal.* **1983**, *19*, 377.

[3] Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353.

[4] Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1596.

[5] Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsy, S. G. *J. Mol. Catal.* **1981**, *13*, 43.

[6] (a) Lin, Y. C.; Milstein, D.; Wreford, S. S. *Organometallics* **1983**, *2*, 1461. (b) Nelson, G. O. *Ibid.* **1983**, *2*, 1474.

[7] **3**: IR (Nujol) 3370 (m, ν_{OH}), 2025 (s, ν_{Ir-H}), 1588 (s, $\nu_{C=O}$), 1570 (s, $\nu_{C=O}$) (IR in solution shows only one band for $\nu_{C=O}$ at 1580 cm^{-1}); ^{1}H NMR (C$_6$D$_6$) δ 2.11 [t, $(J_{PH} + J_{P'H})/2$ = 3 Hz, 18 H, PMe$_3$)], 2.13 (d, J_{PH} = 8 Hz, 9 H, PMe$_3$), 4.36 (d, J = 3 Hz, 2 H, CH$_2$O), 4.68 (t, J = 3 Hz, 1 H, OH), -7.25 (d of t, J_{HP}(trans) = 128, J_{HP}(cis) = 17.8 Hz, 1 H, IrH); upon addition of D$_2$O the triplet at 4.68 disappears and the doublet at 4.36 becomes a singlet; ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 5.65 (t, J = 22.4 Hz, 1 P), 11.43 (d, J = 22.4 Hz, 2 P). Satisfactory C and H analyses were obtained for **3**, **4**, and **8**.

[8] X-ray quality crystals of **3** were obtained from a benzene solution by vapor diffusion of pentane.

[9] Crystal data for **3**: IrC$_{11}$H$_{31}$P$_3$ClO$_2$ space group $\bar{P}1$, No. 2, cell dimensions (-100 °C) a = 14.818 (2) Å, b = 15.150 (2) Å, c = 8.752 (1) Å, α = 93.55 (1)°, β = 95.17 (1)°, γ = 90.77 (1)°, λ = 0.71069 Å, V = 1952.7 Å^3, R = 0.036, R_w = 0.035. All details are included in the supplementary material.

0002-7863/86/1508-1336$01.50/0