2326 Organometallics 1987, 6, 2326-2331

Four-, Five-, or Six-Membered Methanide Auracycles: X-ray Structure of $[(C_6F_5)_2AuPPh_2CH(AuC_6F_5)PPh_2CHCOOMe]$

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Received February 10, 1987

The complexes $[R_2ClAuPPh_2CH_2PPh_2CH_2COOMe]ClO_4$ and $[R_2ClAuSPPh_2CH_2PPh_2CH_2COOMe]ClO_4$ ($R = C_6F_5$) can be deprotonated with $AgClO_4$, Na_2CO_3, or NaH to synthesize four-, five-, or six-membered auracycles: $[R_2AuSPPh_2CHPPh_2CH_2COOMe]ClO_4$, $[R_2AuPPh_2CHPPh_2CHCOOMe]$, $[R_2AuPPh_2CH_2PPh_2CHCOOMe]ClO_4$, or $[R_2AuSPPh_2CHPPh_2CHCOOMe]$. The methanide C atom in these neutral complexes is a nucleophile and can be used as donor atom to form homodinuclear complexes $[R_2Au\{SPPh_2(AuX)PPh_2CHCOOMe\}]$ ($X = C_6F_5$) or $[R_2Au\{PPh_2CH(AuX)PPh_2CHCOOMe\}]$ ($X = Cl$, C_6F_5) or heterodinuclear complexes $[R_2Au\{PPh_2CH(AgPPh_3)PPh_2CHCOOMe\}]ClO_4$. The structure of $[(C_6F_5)_2Au\{PPh_2CH(AuC_6F_5)PPh_2CHCOOMe\}]$ has been solved by X-ray crystallography. It crystallizes in space group $P\bar{1}$ with $a = 12.719$ (5) Å, $b = 12.830$ (5) Å, $c = 17.918$ (7) Å, $\alpha = 70.67$ (3)°, $\beta = 76.11$ (3)°, $\gamma = 72.07$ (3)°, and $Z = 2$.

Introduction

The synthesis of gold(I) or gold(III) methanide complexes by the reaction between precursors of the type $[R_nAuPPh_2CH_2PPh_2R']ClO_4$ and NaH as a deprotonating agent, to give neutral $[R_nAuPPh_2CHPPh_2R']$ ($R_n = C_6F_5$, $(C_6F_5)_2Cl$, $(C_6F_5)_3$; $R' = Me$, $CH_2C_6H_5$, $CH_2C_6F_5$) is well-documented,[1-4] but only single deprotonation of the diphosphine ligand has been observed so far.

Suitable modification of the precursor, i.e., the use of $[(C_6F_5)_2ClAu(PPh_2CH_2PPh_2CH_2COOMe)]^+ClO_4^-$ or $[(C_6F_5)_2ClAu(SPPh_2CH_2PPh_2COOMe)]^+ClO_4^-$, enables the deprotonation of either one or two methylene groups by choice of the reaction conditions: at room temperature and with Na_2CO_3 or $AgClO_4$ as deprotonating agents single deprotonation under simultaneous halide abstraction takes place, leading to the cationic four- or five-membered auracycles $[(C_6F_5)_2Au(SPPh_2CHPPh_2COOMe)]ClO_4$ or $[(C_6F_5)_2Au(PPh_2CH_2PPh_2CHCOOMe)]ClO_4$, while NaH at room temperature or Na_2CO_3 in refluxing chloroform deprotonates both CH_2 groups to give the neutral five- or six-membered auracycles $[(C_6F_5)_2Au(PPh_2CHPPh_2CHCOOMe)]$ or $[(C_6F_5)_2AuSPPh_2CHPPh_2CHCOOMe)]$, whose methanide carbon atoms can serve as electron donors to other metal centers, thus forming homo- or heteronuclear derivatives.

Results and Discussion

The substituted phosphinophosphonium salts were prepared by the following processes (eq 1 and 2).

$$Ph_2PCH_2PPh_2 + ClCH_2COOMe \rightarrow [Ph_2PCH_2PPh_2CH_2COOMe]Cl \xrightarrow{AgClO_4} \underset{\mathbf{1}}{[Ph_2PCH_2PPh_2CH_2COOMe]ClO_4} \quad (1)$$

$$\mathbf{1} + {}^1/_8S_8 \rightarrow \underset{\mathbf{2}}{[SPPh_2CH_2PPh_2CH_2COOMe]ClO_4} \quad (2)$$

Both complexes **1** and **2** react with the dimer $[Au(\mu\text{-}Cl)(C_6F_5)_2]_2$, cleaving the bridges and affording (eq 3) the cationic gold(III) derivatives **3** and **4**.

$$\tfrac{1}{2}[Au(\mu\text{-}Cl)(C_6F_5)_2]_2 + [Ph_2PCH_2PPh_2CH_2COOMe]ClO_4 \text{ or } [SPPh_2CH_2PPh_2CH_2COOMe]ClO_4 \rightarrow \underset{\mathbf{3}}{[(C_6F_5)_2ClAuPPh_2CH_2PPh_2CH_2COOMe]ClO_4} \text{ or } \underset{\mathbf{4}}{[(C_6F_5)_2ClAuSPPh_2CH_2PPh_2CH_2COOMe]ClO_4} \quad (3)$$

At room temperature, NaH reacts with complexes **3** or **4** in dichloromethane solution to give five- or six-membered auracycles (see Schemes I and II) as the result of the precipitation of the perchlorato anion and the chloride ligand (as the sodium salts) and the simultaneous deprotonation of both CH_2 groups with evolution of molecular hydrogen.

Analogous results (complexes **5** or **6**) are obtained by reaction of complexes **3** or **4** with Na_2CO_3 in refluxing chloroform (albeit without H_2 evolution, $NaHCO_3$ being formed instead).

At room temperature, dichloromethane solutions of complex **3** also react with Na_2CO_3, but only the CH_2 group α to the COOMe moiety undergoes deprotonation and as a result the cationic five-membered auracycle $[(C_6F_5)_2AuPPh_2CH_2PPh_2CHCOOMe]ClO_4$ (**7**) is obtained. The same complex **7** can also be obtained by reaction of complex **3** with $AgClO_4$ (eq 5), the enhanced acidity of the CH_2 group α to COOMe outweighing that of the perchloric acid.

$$[(C_6F_5)_2ClAuPPh_2CH_2PPh_2CH_2COOMe]ClO_4 \xrightarrow{AgClO_4} AgCl + HClO_4 + \mathbf{7} \quad (5)$$

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[1] Usón, R.; Laguna, A.; Laguna, M.; Manzano, B. R.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 839.

[2] Usón, R.; Laguna, A.; Laguna, M.; Lázaro, I.; Morata, A.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 669.

[3] Laguna, A.; Laguna, M.; Rojo, A.; Fraile, M. N. *J. Organomet. Chem.* **1986**, *315*, 269.

[4] Usón, R.; Laguna, A.; Laguna, M.; Lázaro, I.; Tartón, M. T. *J. Chem. Soc., Dalton Trans.* in press.

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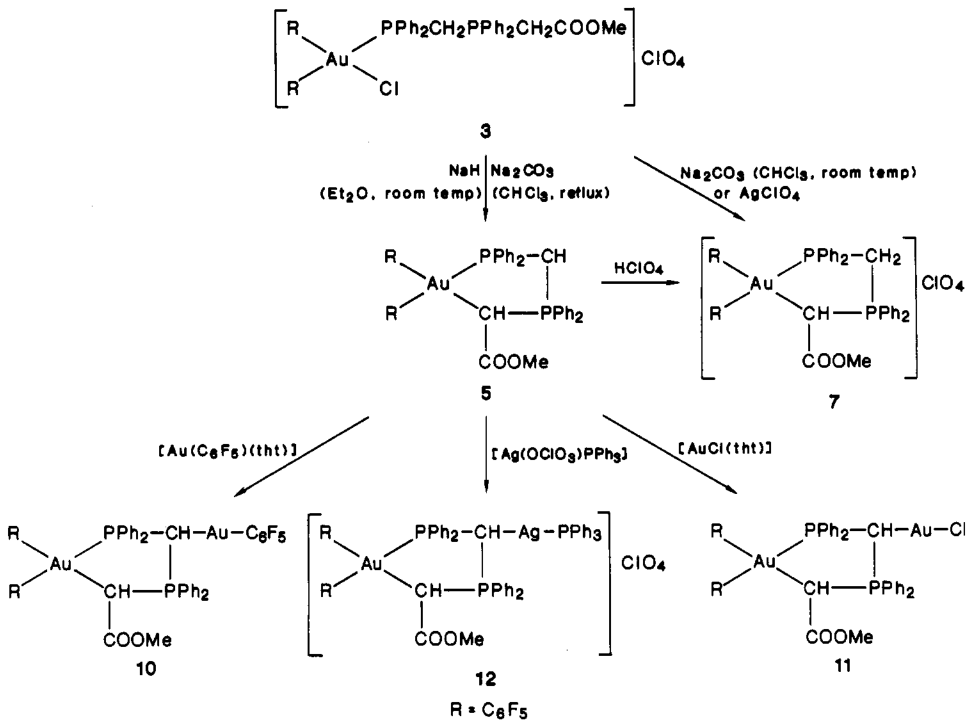
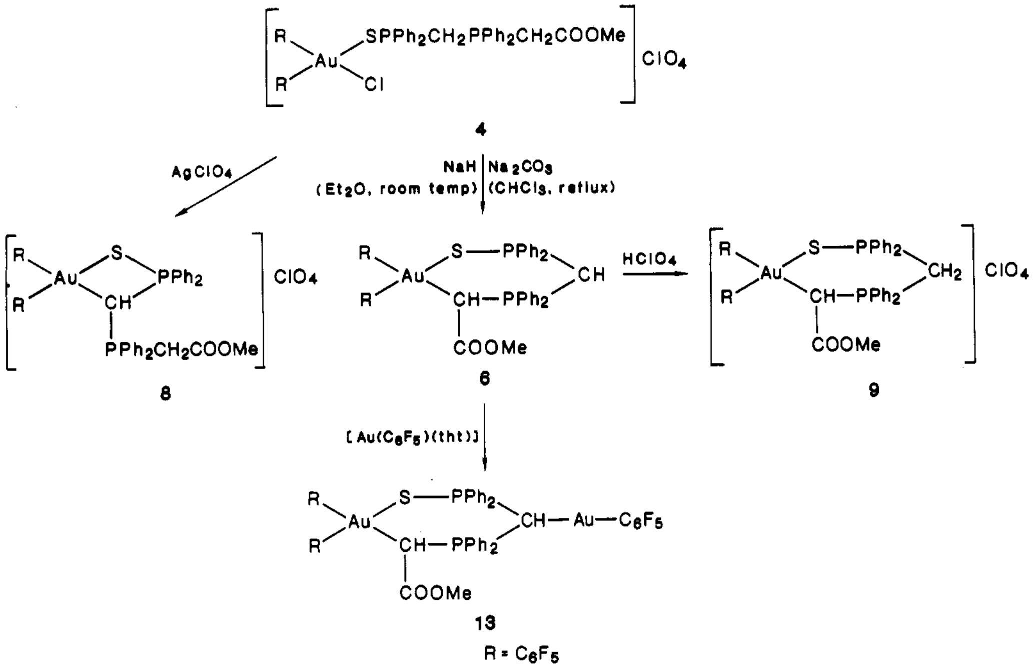
Scheme I



Scheme II



At room temperature, dichloromethane solutions of complex **4** react with $AgClO_4$ to deprotonate the CH_2 bridge between the two P atoms and form a cationic four-membered auracycle $[(C_6F_5)_2AuSPPh_2CHPPh_2CH_2COOMe]ClO_4$ (**8**), the presence of the S atom also enhancing the acidity of the nearest CH_2 group. Dichloromethane solutions of complex **4** react with Na_2CO_3 at room temperature to give mixtures of complexes **6** and **8**, as can be inferred from the IR and NMR spectra (see below).

Complexes **5** and **6** react (1:1) with $HClO_4$ to give complex **7** or $[(C_6F_5)_2AuSPPh_2CH_2PPh_2CHCOOMe]ClO_4$ (**9**); i.e., the methanide CH group undergoes protonation and cationic complexes result.

The basic nature of the methanide CH groups in complexes **5** and **6** can also be demonstrated through the reactions of these complexes with other metal centers containing one weakly coordinating ligand (e.g., $[Au(C_6F_5)(tht)]$, $[AuCl(tht)]$, $[Ag(OClO_3)PPh_3]$) which afford homo- or heterobinuclear derivatives (complexes **10**–**13**, see Schemes I and II). The structure of $[(C_6F_5)_2Au\{PPh_2CH(AuC_6F_5)PPh_2CHCOOMe\}]$ (**10**) has been established by X-ray crystallography (Figure 1). Coordination geometry and molecular dimensions are as expected; in particular, bond lengths and angles at the methanide groups are in good agreement with those observed in related complexes.[1,2] The relative configurations at C(1) and C(2) are *RR* (and *SS*, both mirror images are present in

Table I. Analytical and Physical Data for Complexes 1-13

complex	yield, %	anal. found (calcd) C	H	Au or Au + Ag	Λ_M[a]	mp,[c] °C	mol wt found (calcd)	ν(CO),[d] cm^{-1}
1, $[PPh_2CH_2PPh_2CH_2COOMe]ClO_4$	88	60.0 (60.4)	4.7 (4.9)		121	129		1730
2, $[SPPh_2CH_2PPh_2CH_2COOMe]ClO_4$	90	56.8 (57.1)	4.65 (4.6)		133	154		1720
3, $[R_2ClAuPPh_2CH_2PPh_2CH_2COOMe]ClO_4$	87	42.9 (42.75)	2.55 (2.4)	17.8 (17.55)	118	183		1735
4, $[R_2ClAuSPPh_2CH_2PPh_2CH_2COOMe]ClO_4$	78	41.65 (41.6)	2.5 (2.35)	17.15 (17.05)	130	166		1730
5, $[R_2AuPPh_2CHPPh_2CHCOOMe]$	83	48.7 (48.7)	2.85 (2.55)	20.65 (19.95)	10	205	939 (986)	1715
6, $[R_2AuSPPh_2CHPPh_2CHCOOMe]$	75	46.85 (47.15)	2.7 (2.45)	19.75 (19.35)	15	206 dec	964 (1018)	1715
7, $[R_2AuPPh_2CH_2PPh_2CHCOOMe]ClO_4$	88	44.4 (44.2)	2.55 (2.4)	18.5 (18.1)	120	238 dec		1725
8, $[R_2AuSPPh_2CHPPh_2CH_2COOMe]ClO_4$	65	43.15 (42.95)	2.5 (2.35)	17.1 (17.6)	101[b]	194 dec		1735
9, $[R_2AuSPPh_2CH_2PPh_2CHCOOMe]ClO_4$	58	42.6 (42.95)	2.35 (2.35)	18.15 (17.6)	117[b]	163		1670
10, $[R_2Au\{PPh_2CH(AuC_6F_5)PPh_2CHCOOMe\}]$	78	40.7 (40.9)	1.8 (1.85)	29.2 (29.15)	2	233	1310 (1350)	1685
11, $[R_2Au\{PPh_2CH(AuCl)PPh_2CHCOOMe\}]$	81	39.25 (39.4)	2.15 (2.05)	33.0 (32.3)	5	178 dec	1231 (1219)	1710
12, $[R_2Au\{PPh_2CH(AgPPh_3)PPh_2CHCOOMe\}]ClO_4$	82	47.9 (47.85)	2.85 (2.75)	21.4 (20.95)	128	214 dec		1690
13, $[R_2Au\{SPPh_2CH(AuC_6F_5)PPh_2CHCOOMe\}]$	70	39.85 (39.95)	2.05 (1.8)	27.95 (28.5)	2	124	1306 (1385)	1700

[a] In acetone (c 5.10^{-4} M); Ω^{-1} cm^2 mol^{-1}. [b] In nitromethane. [c] Or decomposition. [d] In Nujol mulls.

Table II. NMR Data

compound	^{1}H NMR[a] P–CH$_2$–P or P–CH–P	P–CH$_2$–CO or P–CH–CO	Me	^{31}P{^{1}H} NMR[c] Au–P or Au–S–P	C–P–C	Ag–PPh$_3$
1, $[PPh_2CH_2PPh_2CH_2COOMe]ClO_4$	4.65 m	4.21 d (13.3)	3.43 s	21.91 s, br	21.91 s, br	
2, $[SPPh_2CH_2PPh_2CH_2COOMe]ClO_4$	4.75 dd (12.2, 15.6)	4.65 d (12.9)	3.60 s	33.71 d	20.49 d (8.5)	
3, $[R_2ClAuPPh_2CH_2PPh_2CH_2COOMe]ClO_4$	5.14 dd (14, 18.2)	4.29 d (13)	3.64 s	16.99 m	21.63 d (14.6)	
4, $[R_2ClAuSPPh_2CH_2PPh_2CH_2COOMe]ClO_4$	5.61 "t" (15.2)	4.38 d (13.3)	3.57 s	39.41 d	21.13 d (14.4)	
5, $[R_2AuPPh_2CHPPh_2CHCOOMe]$	2.06 dd (18.2)[b]	3.68 d (4.8)	3.11 s	33.66 dm	42.63 d (96.6)	
6, $[R_2AuSPPh_2CHPPh_2CHCOOMe]$	3.51 "t" (8.8)	4.20 d (3.7)	3.03 s	39.12 d	36.13 d (4.7)	
7, $R_2AuPPh_2CH_2PPh_2CHCOOMe]ClO_4$	4.99 "dt", 5.61 "dt"[e]	4.13 d (1.8)	3.62 s	29.94 m	44.92 d (42.8)	
8, $[R_2AuSPPh_2CHPPh_2CH_2COOMe]ClO_4$	3.09 dd (11.8, 16.2)	4.01 "dd", 4.32 "t"[e]	3.34 s	58.90 d	24.54 d (12.9)	
9, $[R_2AuSPPh_2CH_2PPh_2CHCOOMe]ClO_4$	4.97 "q", 5.50 "q"[e]	3.41 d (6.4)	3.23 s	35.85 d	24.33 d (12.7)	
10, $[R_2Au\{PPh_2CH(AuC_6F_5)PPh_2CHCOOMe\}]$	4.04 dd (15.8, 20.9)	4.18 dd (3.5, 4.7)	3.48 s	40.98 dm	52.44 d (49.7)	
11, $[R_2Au\{PPh_2CH(AuCl)PPh_2CHCOOMe\}]$	4.51 dd (15.7, 20.9)	4.05 dd (3.2, 4.4)	3.47 s	37.61 dm	48.59 d (53.2)	
12, $[R_2Au\{PPh_2CH(AgPPh_3)PPh_2CHCOOMe\}]ClO_4$	4.98 m	3.93 s, br	3.38 s	34.02 dm	49.87 d (54)	14.66 dd (579, 667)[d]
13, $[R_2Au\{SPPh_2CH(AuC_6F_5)PPh_2CHCOOMe\}]$	4.38 "t" (18.2)	3.28 d (6.5)	3.43 s	42.95 d	28.15 d (7.8)	

[a] Recorded in $CDCl_3$ at 200 MHz referenced to internal TMS; δ (J_{P-H} in Hz); s = singlet, d = doublet, "t" = apparent triplet, "q" = apparent quartet, dd = doublet of doublet, dm = doublet of multiplet, m = multiplet, br = broad. [b] Part X of an ABX system, so the number in parentheses is the sum of J_{AX} and J_{BX}. [c] Referenced to external H_3PO_4. [d] $J_{P-^{107}Ag}$ and $J_{P-^{109}Ag}$. [e] See text.

the crystal).

Complexes **1**–**4** and **7**–**13** are air- and moisture-stable white solids. The methanides **5** and **6** are yellow solids, and the latter must be preserved under dry nitrogen. The cationic derivatives **3**, **4**, **7**–**9**, and **12** behave as 1:1 electrolytes (in acetone or nitromethane solutions),[5] and their IR spectra show bands at 1100 (s, br) and 620 (m) cm^{-1}, which are characteristic of the ClO_4^- anion.[6] In contrast, acetone solutions of complexes **5**, **6**, **10**, **11**, and **13** are nonconducting; the molecular weights of these complexes (isopiestic, in chloroform) are in good agreement with the expected values.

Two strong bands in the 800 cm^{-1} region confirm that both C_6F_5 groups in complexes **3**–**13** are mutually cis;[7] ν(Au–Cl)[8] is observed at 330 (**3**), 320 (**4**), or 325 cm^{-1} (**11**). The methanide group in complexes **5** and **6** gives rise to strong absorptions[4] (at 1210 and 1250 cm^{-1} for **5** and at 1210 and 1255 cm^{-1} for **6**) which are absent after protonation of this group with $HClO_4$ (complexes **7** and **9**) or after coordination to a gold or silver center (complexes **10**–**13**).

The ν(CO) vibration[9] in ligands **1** and **2** is not very sensitive to the different situations in complexes **3**–**13** (Table I).

Table II presents ^{1}H NMR data for the complexes (the

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(5) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(6) Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc.* **1961**, 3091.

(7) Usón, R.; Laguna, A.; García, J.; Laguna, M. *Inorg. Chim. Acta* **1979**, *37*, 201.

(8) Usón, R.; Laguna, A.; Vicente, J. *Rev. Acad. Cienc. Exactas Fis. Quim. Nat., Zaragoza* **1976**, *31*, 211.

(9) Vicente, J.; Chicote, M. T.; Cayuelas, J. A.; Fernández-Baeza, J.; Jones, P. G.; Sheldrick, G. M.; Espinet, P. *J. Chem. Soc., Dalton Trans.* **1985**, 1163.

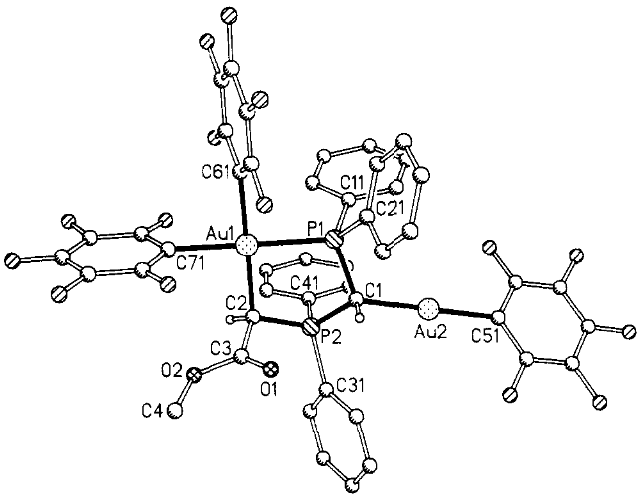

Figure 1. Molecular structure of complex **10**, showing the atom-numbering scheme (phenyl H's omitted; the radii arbitrary). The relative configurations at C(1) and C(2) are *RR*.

phenylic protons, which appear as multiplets between 7 and 8 ppm and are in agreement with the proposed formula, are omitted) that distinguish the site of single deprotonation. Thus, the resonances due to the moieties $\mathrm{P{-}CH_2{-}P}$ or P–CH–P generally appear as double doublets, pseudotriplets "t", or triplets as a consequence of the coupling with the P atoms. Although the ylidic carbon atoms are chiral centers when coordinated to the gold atom (complexes **5–13**), the NMR spectra do not permit decision between *R* and *S* enantiomers. The $\mathrm{P{-}CH_2{-}P}$ moiety, in complexes **7** and **9**, behaves as a ABXY system that appears as a deceptively simple spectrum, each signal giving rise to an apparent doublet of triplets or to an apparent quartet, which have not been analyzed. Moreover, the group $\mathrm{(P{-}CH{-}P)AgPPh_3}$ (complex **12**) appears as a multiplet by coupling with the P atoms and with $^{107}\mathrm{Ag}$ and $^{109}\mathrm{Ag}$.

The group $\mathrm{P{-}CH_2{-}CO}$ in complexes **3** and **4** gives rise to doublets with $^2J_{\mathrm{P-H}} > 10$ Hz. In complex **8** both protons are inequivalent and appear as the deceptively simple ABXY system. Deprotonation and subsequent bonding to the Au(III) center shift the signal to higher fields as a doublet with $^2J_{\mathrm{P-H}} < 6.5$ Hz and $^4J_{\mathrm{P-H}} = 0$; in complexes **10** and **11** the latter constant is nonzero and the signal is a doublet of doublets. The $\mathrm{CH_3}$ group resonates as a singlet in all cases.

The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra show two coupled P atoms in all cases except complex **1** which shows only one signal (even at −50 °C) at 21.91 (s, br) ppm, while the precursor $[\mathrm{PPh_2CH_2PPh_2CH_2COOMe}]\mathrm{Cl}$ shows two doublets at 24.68 and −26.32 ppm, $J_{\mathrm{P-P}} = 65$ Hz, in agreement with previous observations for the reported bromide derivative.[10] In complexes **3**, **5**, **7**, and **10–12**, with a direct Au–P bond, coupling with the fluorine nuclei of the trans $\mathrm{C_6F_5}$ group gives rise to a doublet of multiplets, confirming the cis stereochemistry. In complex **8** the signal at a lower field (58.90 ppm) confirms its structure as a four-membered auracycle (compare[3] with 69.56 ppm in the similar $[(\mathrm{C_6F_5})_2\mathrm{AuSPPh_2CHPPh_2S}]$ compound).

Since each of the complexes **10–13** has two chiral centers, four isomers are possible in each case. Since the single and sharp methyl resonance and the simple $^{31}\mathrm{P}\{^1\mathrm{H}\}$ spectra rule out the presence of diastereomers, we have in our samples either only one isomer or an enantiomeric mixture (see above, structure of complex **10**).

Experimental Section

Instrumentation and general experimental techniques were as described earlier.[2] The yields, melting points, C, H, and Au analyses, conductivities, molecular weights, and ν(CO) of the novel complexes are listed in Table I. $^1\mathrm{H}$ and $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR data are listed in Table II. All the reactions were run at room temperature if not mentioned otherwise.

Preparation of the Ligands. $[\mathrm{Ph_2PCH_2PPh_2CH_2COOMe}]\mathrm{ClO_4}$ (1). To a solution of $\mathrm{Ph_2PCH_2PPh_2}$ (1.15 g, 3 mmol) in 15 mL of chloroform was added $\mathrm{ClCH_2COOMe}$ (0.33 mL, 3.6 mmol), and the mixture was stirred for 5 days; then the solution was evaporated to ca. 5 mL, and addition of $\mathrm{Et_2O}$ (15 mL) led to precipitation of $[\mathrm{Ph_2PCH_2PPh_2CH_2COOMe}]\mathrm{Cl}$ as a white solid, 85% yield. To a solution of the chloride (0.986 g, 2 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL) was added $\mathrm{AgClO_4}$ (0.415 g, 2 mmol), and the mixture was stirred for 6 h. The AgCl formed was filtered off, and the solution was evaporated to ca. 5 mL; addition of $\mathrm{Et_2O}$ (15 mL) gave **1** as a white solid (95%).

$[\mathrm{SPPh_2CH_2PPh_2CH_2COOMe}]\mathrm{ClO_4}$ (2). To a suspension of **1** (1.11 g, 2 mmol) in toluene (30 mL) was added $\mathrm{S_8}$ (0.16 g, 0.62 mmol), and the mixture was stirred for 6 h at reflux temperature. The resulting white solid was filtered off, washed with $\mathrm{CS_2}$ (3 × 3 mL), and recrystallized from $\mathrm{CH_2Cl_2/Et_2O}$ (90%).

Preparation of the Complexes. $[\mathrm{R_2ClAuPPh_2CH_2PPh_2CH_2COOMe}]\mathrm{ClO_4}$ (3) and $[\mathrm{R_2ClAuSPPh_2CH_2PPh_2CH_2COOMe}]\mathrm{ClO_4}$ (4). To a suspension of $[\mathrm{Au}(\mu\text{-}\mathrm{Cl})(\mathrm{C_6F_5})_2]_2$[11] (0.227 g, 0.2 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL) was added **1** (0.223 g, 0.4 mmol) or **2** (0.236 g, 0.4 mmol). After 3 h of stirring, a slight turbidity was removed by filtration through a layer of Kieselguhr (1 cm). Concentration to ca. 5 mL and addition of $\mathrm{Et_2O}$ (15 mL) led to the precipitation of complexes **3** and **4**, as white solids.

$[\mathrm{R_2AuPPh_2CHPPh_2CHCOOMe}]$ (5) and $[\mathrm{R_2AuSPPh_2CHPPh_2CHCOOMe}]$ (6). (a) A diethyl ether (20 mL) suspension of NaH (0.3 g, 12.5 mmol) and complex **3** (0.337 g, 0.3 mmol) or **4** (0.347 g, 0.3 mmol) was stirred for 3 h. The excess of NaH and the precipitated $\mathrm{NaClO_4}$ and NaCl were filtered off under $\mathrm{N_2}$, and the solution was evaporated to ca. 2 mL; addition of *n*-hexane (10 mL) gave **5** or **6** as yellow solid.

(b) To a solution of **3** (0.11 g, 0.1 mmol) or **4** (0.115 g, 0.1 mmol) in $\mathrm{CHCl_3}$ (20 mL) was added $\mathrm{Na_2CO_3}$ (0.3 g, 2.8 mmol), and the mixture was stirred for 2 h at reflux temperature. The excess of $\mathrm{Na_2CO_3}$ and the precipitated $\mathrm{NaClO_4}$ and NaCl were filtered off under $\mathrm{N_2}$, and the solution was evaporated to ca. 1 mL; addition of *n*-hexane (10 mL) gave **5** or **6**, respectively.

$[\mathrm{R_2AuPPh_2CH_2PPh_2CHCOOMe}]\mathrm{ClO_4}$ (7). This complex can be obtained in different ways.

(a) To a yellow solution of **5** (0.197 g, 0.2 mmol) in $\mathrm{Et_2O}$ (15 mL) was added $\mathrm{HClO_4}$ (0.022 mL of 9.198 M solution, 0.2 mmol). The solution turned immediately white, whereby a white solid (**7**) precipitated and was filtered off (88%).

(b) To a solution of **3** (0.225 g, 0.2 mmol) in dichloromethane (20 mL) was added $\mathrm{Na_2CO_3}$ (0.3 g, 2.8 mmol), and the mixture was stirred for 3 h. The excess of $\mathrm{Na_2CO_3}$ and the precipitated NaCl were filtered off, and the solution was evaporated to 2 mL; addition of $\mathrm{Et_2O}$ gave **7** (70%).

(c) To a solution of **3** (0.225 g, 0.2 mmol) in dichloromethane (20 mL) was added $\mathrm{AgClO_4}$ (0.042 g, 0.2 mmol), and the mixture was stirred for 8 h. Working as described in method b, **7** (85%) was obtained.

$[\mathrm{R_2AuSPPh_2CHPPh_2CH_2COOMe}]\mathrm{ClO_4}$ (8). Working as described for **7**, method c, but starting from **4** (0.231 g, 0.2 mmol), gave **8**.

$[\mathrm{R_2AuSPPh_2CH_2PPh_2CHCOOMe}]\mathrm{ClO_4}$ (9). Working as described for **7**, method a, but starting from **6** (0.204 g, 0.2 mmol), gave **9**.

$[\mathrm{R_2Au\{PPh_2CH(AuX)PPh_2CHCOOMe\}}]$ [X = $\mathrm{C_6F_5}$ (10), Cl

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(10) Oosawa, Y.; Urabe, H.; Saito, T.; Sasaki, Y. *J. Organomet. Chem.* **1976**, *122*, 113.

(11) Usón, R.; Laguna, A.; Laguna, M.; Abad, M. *J. Organomet. Chem.* **1983**, *249*, 437.

Table III. Atom Coordinates ($\times 10^4$) and Isotropic Temperature Factors ($Å^2 \times 10^3$) for Compound 10

	x	*y*	*z*	*U*
Au(1)	4160 (1)	6339 (1)	2422.5 (.5)	44 (1)[a]
Au(2)	8219 (1)	4176 (1)	3243.5 (.5)	46 (1)[a]
P(1)	6067 (5)	6134 (5)	2415 (3)	42 (3)[a]
P(2)	5761 (5)	3883 (5)	3178 (3)	43 (3)[a]
C(12)	7989 (11)	5953 (12)	1296 (8)	55 (6)
C(13)	8612	5806	567	72 (8)
C(14)	8096	5706	−2	82 (8)
C(15)	6956	5752	159	69 (7)
C(16)	6332	5900	888	53 (6)
C(11)	6849	6000	1457	42 (6)
C(22)	6283 (13)	7290 (13)	3426 (8)	77 (8)
C(23)	6489	8201	3579	99 (10)
C(24)	6759	9108	2945	95 (9)
C(25)	6822	9104	2158	84 (9)
C(26)	6616	8194	2005	64 (7)
C(21)	6346	7287	2639	51 (6)
C(32)	6356 (13)	2726 (11)	4689 (9)	67 (7)
C(33)	6586	1766	5337	83 (8)
C(34)	6482	721	5326	92 (9)
C(35)	6148	636	4666	99 (10)
C(36)	5918	1596	4017	80 (8)
C(31)	6022	2641	4029	48 (6)
C(42)	5429 (10)	3266 (13)	1919 (9)	81 (8)
C(43)	5783	2873	1239	77 (8)
C(44)	6920	2602	933	68 (7)
C(45)	7701	2723	1307	86 (9)
C(46)	7346	3116	1987	68 (7)
C(41)	6210	3387	2293	40 (5)
C(51)	9906 (10)	3555 (13)	3329 (10)	59 (7)
C(52)	10667	3625	2620	84 (9)
C(53)	11810	3185	2648	109 (11)
C(54)	12193	2676	3384	65 (7)
C(55)	11432	2606	4093	78 (8)
C(56)	10289	3045	4066	64 (7)
C(61)	3957 (13)	8050 (11)	1717 (9)	49 (6)
C(62)	3915	8352	900	74 (8)
C(63)	3783	9490	449	76 (8)
C(64)	3691	10326	815	123 (12)
C(65)	3732	10024	1632	95 (9)
C(66)	3865	8886	2084	64 (7)
C(71)	2465 (9)	6527 (12)	2413 (9)	40 (5)
C(72)	1657	6923	3004	49 (6)
C(73)	529	7035	3010	85 (9)
C(74)	209	6752	2424	85 (9)
C(75)	1016	6356	1833	82 (8)
C(76)	2144	6244	1828	73 (8)
C(1)	6492 (17)	4885 (17)	3174 (12)	50 (6)
C(2)	4330 (17)	4650 (17)	3168 (11)	47 (6)
C(3)	3738 (18)	4723 (18)	4009 (12)	52 (6)
C(4)	2020 (22)	4711 (22)	4925 (16)	79 (8)
O(1)	4111 (13)	4975 (13)	4457 (9)	69 (5)
O(2)	2713 (13)	4526 (13)	4180 (9)	66 (5)
F(52)	10360 (13)	3973 (17)	1924 (8)	144 (11)[a]
F(53)	12571 (14)	3226 (17)	1989 (10)	157 (12)[a]
F(54)	13279 (11)	2222 (14)	3417 (11)	123 (11)[a]
F(55)	11806 (13)	2106 (15)	4788 (10)	124 (11)[a]
F(56)	9589 (11)	2948 (14)	4733 (7)	97 (8)[a]
F(62)	3975 (13)	7595 (13)	533 (8)	92 (9)[a]
F(63)	3728 (16)	9768 (17)	−334 (9)	152 (12)[a]
F(64)	3593 (18)	11427 (14)	375 (13)	173 (14)[a]
F(65)	3676 (19)	10840 (16)	1969 (13)	164 (14)[a]
F(66)	3869 (12)	8607 (11)	2860 (7)	83 (8)[a]
F(72)	1945 (11)	7234 (13)	3536 (8)	87 (8)[a]
F(73)	−249 (13)	7396 (17)	3553 (12)	135 (12)[a]
F(74)	−857 (12)	6876 (18)	2422 (14)	166 (15)[a]
F(75)	747 (17)	6129 (20)	1255 (14)	186 (17)[a]
F(76)	2923 (12)	5768 (14)	1301 (9)	105 (10)[a]

[a] Equivalent isotropic *U* calculated from anisotropic *U*.

(11)]. To a solution of **5** (0.197 g, 0.2 mmol) in diethyl ether (20 mL) was added $[Au(C_6F_5)(tht)]$[12] (0.090 g, 0.2 mmol) or [AuCl(tht)][11] (0.060 g, 0.2 mmol). After 4 h of stirring, the solution was evaporated to ca. 5 mL and addition of hexane (20 mL) gave **10**. Under analogous conditions, using [AuCl(tht)], complex **11** precipitated and was filtered off.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for Compound 10

	Bond Lengths		
Au(1)–P(1)	2.354 (7)	Au(1)–C(61)	2.111 (13)
Au(1)–C(71)	2.098 (14)	Au(1)–C(2)	2.113 (20)
Au(2)–C(51)	2.071 (14)	Au(2)–C(1)	2.119 (21)
C(11)–P(1)	1.798 (15)	C(21)–P(1)	1.805 (22)
C(31)–P(2)	1.813 (15)	C(41)–P(2)	1.803 (20)
C(1)–P(1)	1.756 (20)	C(1)–P(2)	1.802 (28)
C(2)–P(2)	1.784 (21)	C(2)–C(3)	1.534 (30)
C(3)–O(1)	1.192 (36)	C(3)–O(2)	1.348 (31)
C(4)–O(2)	1.460 (31)		
	Bond Angles		
P(1)–Au(1)–C(61)	91.9 (6)	P(1)–Au(1)–C(71)	179.3 (5)
C(61)–Au(1)–C(71)	87.7 (7)	P(1)–Au(1)–C(2)	88.7 (7)
C(61)–Au(1)–C(2)	177.7 (8)	C(71)–Au(1)–C(2)	91.7 (8)
C(51)–Au(2)–C(1)	177.0 (10)	Au(1)–P(1)–C(11)	109.6 (7)
Au(1)–P(1)–C(21)	114.0 (6)	C(11)–P(1)–C(21)	109.2 (9)
Au(1)–P(1)–C(1)	106.2 (9)	C(11)–P(1)–C(1)	110.5 (9)
C(21)–P(1)–C(1)	107.2 (12)	C(31)–P(2)–C(41)	107.1 (9)
C(31)–P(2)–C(1)	109.3 (11)	C(41)–P(2)–C(1)	112.8 (10)
C(31)–P(2)–C(2)	115.0 (9)	C(41)–P(2)–C(2)	106.8 (10)
C(1)–P(2)–C(2)	105.8 (12)	Au(2)–C(1)–P(1)	119.6 (12)
Au(2)–C(1)–P(2)	114.1 (11)	P(1)–C(1)–P(2)	107.0 (14)
Au(1)–C(2)–P(2)	111.9 (12)	Au(1)–C(2)–C(3)	107.1 (15)
P(2)–C(2)–C(3)	111.3 (16)	C(2)–C(3)–O(1)	124.4 (22)
C(2)–C(3)–O(2)	112.6 (23)	O(1)–C(3)–O(2)	122.9 (20)
C(3)–O(2)–C(4)	117.3 (23)		

$[R_2Au\{PPh_2CH(AgPPh_3)PPh_2CHCOOMe\}]ClO_4$ (12). To a solution of **5** (0.197 g, 0.2 mmol) in dichloromethane (20 mL) was added $[Ag(OClO_3)PPh_3]$[13] (0.094 g, 0.2 mmol), and the mixture was stirred for 1 h. Evaporation to ca. 5 mL and addition of diethyl ether (20 mL) gave **12**.

$[R_2Au\{SPPh_2CH(AuC_6F_5)PPh_2CHCOOMe\}]$ (13). To a solution of **6** (0.204 g, 0.2 mmol) in diethyl ether (20 mL) was added $[Au(C_6F_5)(tht)]$ (0.090 g, 0.2 mmol)], and the mixture was stirred for 2 h. Partial concentration to ca. 5 mL and addition of hexane gave **13**.

Crystal Structure Determination of Compound 10. Crystal data: $C_{46}H_{25}AuF_{15}O_2P_2$: M_r 1350.56; triclinic; $P\bar{1}$; $a = 12.719$ (5) Å, $b = 12.830$ (5) Å, $c = 17.918$ (7) Å; $\alpha = 70.67$ (3)°, $\beta = 76.11$ (3), $\gamma = 72.07$ (3)°; $U = 2594$ Å^3; $Z = 2$, $D_{calcd} = 1.73$ g cm^{-3}, $F(000) = 1280$, Mo Kα; $\lambda_{\bar{\alpha}} = 0.71069$ Å; μ(Mo Kα) = 5.8 mm^{-1}. Colorless sphenoidal crystals were grown by diffusion of hexane into a solution of **10** in 1,2-dichloroethane. A crystal with dimensions 0.4 × 0.2 × 0.15 mm was used to measure 9888 profile-fitted intensities[14] on a Stoe-Siemens four-circle diffractometer ($2\theta_{max} \geq 45°$). Absorption corrections were based on ψ scans. Of 6761 unique reflections, 4053 with $F > 4\sigma(F)$ were used for all calculations (program system SHELXTL). Cell constants were refined from 2θ values of 42 reflections in the range 20–23°.

The structure was solved by the heavy-atom method and refined to $R = 0.072$ and $R_w = 0.062$ [Au, P, and F were anisotropic; aromatic rings as rigid hexagons with C–C = 1.395 Å, and C–H (where appropriate) = 0.96 Å; methylide H using riding model; weighting scheme $w^{-1} = \sigma^2(F) + 0.0005F^2$; 280 parameters]. Final atomic coordinates are given in Table III with derived bond lengths and angles in Table IV.

Acknowledgment. We thank the DGA for the award of a fellowship to I.L. and the CAICYT and the Fonds der Chemischen Industrie for financial support.

Registry No. **1**, 110317-28-7; **2**, 110317-30-1; **3**, 110317-11-8; **4**, 110317-13-0; **5**, 110317-14-1; **6**, 110317-15-2; **7**, 110317-17-4; **8**,

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(12) Usón, R.; Laguna, A.; Vicente, J. *J. Organomet. Chem.* **1977**, *131*, 471.

(13) Cotton, F. A.; Falvello, L. R.; Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Ara, I. *Inorg. Chem.* **1987**, *26*, 1366.

(14) Clegg, W. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1981**, *A37*, 22.

110317-19-6; **9**, 110317-21-0; **10**, 110317-22-1; **11**, 110317-23-2; **12**, 110317-26-5; **13**, 110317-24-3; $[Au(\mu\text{-}Cl)(C_6F_5)_2]_2$, 87105-61-1; $[Au(C_6F_5)(tht)]$, 60748-77-8; $[AuCl(tht)]$, 39929-21-0; $[Ag(OClO_3)PPh_3]$, 73165-02-3; $[Ph_2PCH_2PPh_2CH_2COOMe]Cl$, 110317-31-2.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, bond lengths, and bond angles (4 pages); a listing of structure factor amplitudes (40 pages). Ordering information is given on any current masthead page.

Reactivity of a Labile Molybdenocene Olefin Complex with Organic π-Acceptors

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Received February 13, 1987

The reactivity of highly labile molybdenocene (Z)-stilbene complex $Cp_2Mo[\eta^2\text{-}(Z)\text{-}C_6H_5CH{=}CHC_6H_5]$ (**1**) ($Cp = \eta^5\text{-}C_5H_5$) with organic acceptor molecules has been investigated. **1** reacts readily with various olefinic and heteroolefinic ligands L to give molybdenocene complexes of the formula Cp_2MoL (L = formaldehyde, nonenolizable ketones, benzalanilide, and thiobenzophenone). Spectroscopic data indicate dihapto coordination of L at the Cp_2Mo fragment via C=C, C=N, C=O, and C=S bonds. Protic substances and some strong acceptors induce a Z–E isomerization of coordinated (Z)-stilbene in **1**, resulting in the formation of the (E)-stilbene complex $Cp_2Mo[\eta^2\text{-}(E)\text{-}C_6H_5CH{=}CHC_6H_5]$ (**2**) which is significantly less labile than the (Z)-stilbene complex. Maleic anhydride catalyzes this isomerization reaction rapidly and cleanly. Extremely electrophilic ketones R_2CO (R = $CO_2C_2H_5$, CF_3) are head-to-head coupled at the divalent molybdenum center of **1** to afford molybdenocene diolato complexes $Cp_2Mo(O_2C_2R_4)$ exclusively. The reaction of **1** with 9,10-phenanthrenequinone gives the enediolato complex $Cp_2Mo(O_2C_{14}H_8)$ of which the oxidation electrochemistry was studied.

Introduction

The metallocene of molybdenum Cp_2Mo ($Cp = \eta^5\text{-}C_5H_5$) was electronically and structurally characterized by infrared, ultraviolet–visible, and magnetic circular dichroism spectra using matrix isolation methods.[2] The 16-electron species molybdenocene has previously been postulated as a reactive intermediate in the two-electron reduction of molybdenocene dichloride Cp_2MoCl_2,[3] the reductive elimination of alkane RH from an alkyl hydride $Cp_2MoR(H)$,[4,5] the photolysis of the carbonyl Cp_2MoCO,[6] and the photoelimination of dihydrogen from the dihydride Cp_2MoH_2.[7] In the presence of two-electron ligands L these reactions give low-valent molybdenocene complexes of the type Cp_2MoL, whereas in the absence of any suitable ligand, a so-called dehydromolybdenocene dimer $[CpMo(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)]_2$ is formed.[8] The reactivity pattern of molybdenocene in solution thus appears to be dominated by an addition reaction of ligand L and by a dimerization reaction which can be viewed as self-insertion of one monomeric molybdenocene unit into the C–H bond of another. With the aid of flash photolysis experiments on the dihydride Cp_2MoH_2, molybdenocene has also been detected as a short-lived species in solution.[9]

Recently, we have described the synthesis and some properties of an unusually labile molybdenocene olefin complex, viz. the (Z)-stilbene adduct of molybdenocene $Cp_2Mo[\eta^2\text{-}(Z)\text{-}C_6H_5CH{=}CHC_6H_5]$ (**1**). Its high reactivity has been utilized for the preparation of acetylene complexes of molybdenocene $Cp_2Mo(\eta^2\text{-}RC{\equiv}CR')$ in a very general way.[10] The observation that the olefinic ligand in **1** is very easily lost giving the dimerization product of molybdenocene and that various acetylenes $RC{\equiv}CR'$ replace (Z)-stilbene under mild conditions suggested to us to regard the (Z)-stilbene complex **1** as a synthetically useful versatile functional equivalent of monomeric molybdenocene. In order to explore further the reactivity of **1**, we investigated its reaction with a selection of organic substrates functioning as good π-acceptors such as olefins and heteroolefins. Since metal–ligand bonding in Cp_2MoL type complexes is mainly stabilized by back bonding from the electron-rich d^4-metal center of the Cp_2Mo fragment to the acceptor orbital of the ligand L,[11] we hoped that with these ligands **1** would easily undergo substitution reactions to give low-valent molybdenocene complexes.

In this paper we wish to report the extension of the ligand replacement reaction leading to a number of new

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(2) (a) Chetwynd-Talbot, J.; Grebenik, P.; Perutz, R. N. *Inorg. Chem.* **1982**, *21*, 3647. (b) Cox, P. A.; Grebenik, P.; Perutz, R. N.; Robinson, M. D.; Grinter, R.; Stern, D. R. *Inorg. Chem.* **1983**, *22*, 3614.

(3) (a) Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1386. (b) Thomas, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 1838. (c) Thomas, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5943. (d) Thomas, J. L. *Inorg. Chem.* **1978**, *17*, 1507.

(4) (a) Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1972**, *94*, 1886. (b) Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1973**, *95*, 7262. (c) Nakamura, A.; Otsuka, S. *J. Mol. Catal.* **1975/76**, *1*, 285.

(5) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 1747.

(6) Wong, K. L. T.; Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1974**, *96*. 3694.

(7) Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1978**, *17*, 2410.

(8) (a) Berry, M.; Cooper, N. J.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 29. (b) Meunier, B.; Prout, K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2558.

(9) Perutz, R. N.; Scaiano, J. C. *J. Chem. Soc., Chem. Commun.* **1984**, 457.

(10) Herberich, G. E.; Okuda, J. *Chem. Ber.* **1984**, *117*, 3112.

(11) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.