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Sulphur-Substituted Alkylpalladium Compounds.
Part 2.* Reactions of Organothiomethyl–palladium Complexes with Proton Acids

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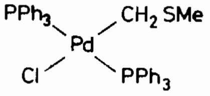
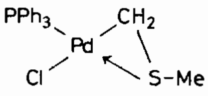
Carbon–palladium bond cleavage occurs on reaction of [(PPh$_2$R)$_2$Pd(CH$_2$SR')X] (R', R = Me or Ph, X = Cl, Br, I or SCN) with excess CF$_3$CO$_2$H or HCl at ambient temperature in CHCl$_3$ solution to give [(PPh$_2$R)$_2$PdX(A)] (A = CF$_3$CO$_2$ or Cl) and MeSR'. With less CF$_3$CO$_2$H, shorter reaction times, or with the weaker acid. CH$_3$CO$_2$H, reversible protonation of the complexes occurs. Complexes, [(PPh$_3$)Pd(CH$_2$SMe)X] (X = Cl, Br or I) containing bidentate CH$_2$SMe' ligands, react more slowly with proton acids (HA) to give halide bridged [(PPh$_3$)-PdX(A)]$_2$ (X = Cl, Br or I; A = Cl or CF$_3$CO$_2$) and Me$_2$S.

Introduction

Organothiomethyl–palladium complexes are known in which the R'SCH$_2$ ligand is monodentate, as in [(PPh$_2$R)$_2$Pd(CH$_2$SR')X] (R = Me or Ph; R' = Me or Ph; X = Cl, Br, I, or SCN), *e.g.* (*I*) or bidentate as in [(PPh$_3$)Pd(CH$_2$SMe)X] (X = Cl, Br, or I) [1, 2], *e.g.* (*II*). Reactions with halogens [1] and some Pd–C insertion reactions [2] of these complexes have been reported. Cleavage of Pd–C sigma bonds in a number of [L$_2$PdR$_2$] and [L$_2$PdRX] compounds by proton acids has variously been shown [3]. We now report details of a protonolysis study of R'SCH$_2$Pd complexes which indicate a significant role for the donor centre, sulphur; a preliminary communication has been published [4].



(*I*)



(*II*)

TABLE I. Proton Chemical Shifts, δCH$_2$, for Interactions of [(PPh$_3$)$_2$Pd(CH$_2$SR)Cl] and CH$_3$CO$_2$H in CDCl$_3$ Solution.

Equivalents of CH$_3$CO$_2$H:	δCH$_2$		
	0	1.0	6.0
[(Ph$_3$P)$_2$Pd(C*H*$_2$SPh)Cl]	2.42	3.04	3.49
[(Ph$_3$P)$_2$Pd(C*H*$_2$SC$_6$H$_4$Me-*p*)Cl]	2.78	3.11	

Experimental

The organopalladium compounds [(PPh$_2$R)$_2$-Pd(CH$_2$SR')X] (R,R' = Me or Ph; X = Cl, Br, I or SCN) and [(PPh$_3$)Pd(CH$_2$SMe)X] (X = Cl, Br or I), were obtained as described previously [1]. Deoxygenated solvents and nitrogen atmospheres were generally used.

Acetic acid, trifluoroacetic acid and hydrogen chloride were the purest grades commercially available, as were other reagents used in this study.

Reactions with Carboxylic Acids

To a solution of the organopalladium compound in CDCl$_3$ (0.18–0.25 *M*), was added, *via* a syringe, known amounts of the carboxylic acid. Interactions were monitored by ^{1}H NMR spectroscopy and g.l.c. Changes in the values of δ(C*H*$_2$) for [(PPh$_2$R)$_n$-Pd(C*H*$_2$SR')X] are listed in Tables I and II for interactions with CH$_3$CO$_2$H and CF$_3$CO$_2$H respectively. Examination by g.l.c. indicated that very little, if any, of the cleavage product (R'SMe) was formed using CH$_3$CO$_2$H or upto 3 equivalents of CF$_3$CO$_2$H and with short reaction times.

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*Part 1. Ref. [1].

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TABLE II. Proton Chemical Shifts, δCH_2, for Interactions of $[(PPh_2R)_nPd(CH_2SR')X]$ and CF_3CO_2H in $CDCl_3$ Solution.

Equivalents of CF_3CO_2H	δCH_2				
	0	0.25	0.50	1.0	2.0
$[(PPh_3)_2Pd(CH_2SPh)Cl]$	2.42	2.78	2.84	3.24	3.30
$[(PPh_3)_2Pd(CH_2SPh)Br]$	2.73	3.05	3.11	3.24	3.16(br)
$[(PPh_3)_2Pd(CH_2SPh)I]$	2.96	2.97	2.98	3.09	3.13
$[(PPh_3)_2Pd(CH_2SPh)SCN]$	2.48	2.64	2.80	3.16	
$[(PPh_3)_2Pd(CH_2SMe)Cl]$	3.26	3.33	3.36	3.36	3.30(br)
$[(PPh_3)_2Pd(CH_2SMe)SCN]$	3.13	3.22	3.24	3.24	3.20(br)
$[(PPh_2Me)_2Pd(CH_2SMe)Cl]$	2.71	2.87	2.98	3.09	3.20
$[(PPh_2Me)_2Pd(CH_2SMe)Br]$	2.98	3.04	3.05	3.08	3.04(br)
$[(PPh_2Me)_2Pd(CH_2SMe)I]$	3.18	3.18	3.19	3.24	3.22
$[(PPh_3)Pd(CH_2SMe)Cl]$	2.68	2.74(br)	2.76(br)	2.80(br)	2.82(br)
$[(PPh_3)Pd(CH_2SMe)Br]$	2.73	2.80[a]	2.80[a]	2.82[a]	2.82[a]
$[(PPh_3)Pd(CH_2SMe)I]$	2.73	2.76	2.80(br)	2.80(br)	2.84(br)

[a] d J 4 Hz.

TABLE III. Products of Reaction of Organopalladium Compounds with Proton Acids.

Organopalladium Reagent	Product	M.p. (°C)	ν (cm^{-1})	Analysis, Calc. (Found)		
				C	H	X
From CF_3CO_2H						
$[(PPh_3)_2Pd(CH_2SPh)Cl]$	$[(PPh_3)_2Pd(OCOCF_3)Cl]$	195–8	322(Pd–Cl) 1680(CO)	58.6 (58.9)	3.9 (4.2)	4.6[Cl] (5.2)
$[(PPh_3)_2Pd(CH_2SPh)Br]$	$[(PPh_3)_2Pd(OCOCF_3)Br]$	180	1670(CO)	55.4 (55.7)	3.7 (3.6)	9.7[Br] (10.0)
$[(PPh_3)_2Pd(CH_2SPh)I]$	$[(PPh_3)_2Pd(OCOCF_3)I]$	130–2	1680(CO)	52.4 (51.2)	3.4 (3.2)	14.6[1] (12.4)
$[(PPh_3)_2Pd(CH_2SPh)SCN]$	$[(PPh_3)_2Pd(OCOCF_3)SCN]$	152–5	1680(CO) 2150(CN)	58.4 (58.0)	3.8 (3.6)	1.8[N] (2.1)
$[(PPh_3)_2Pd(CH_2SMe)Cl]$	$[(PPh_3)_2Pd(OCOCF_3)Cl]$	195–9	320(PdCl) 1680(CO)	58.6 (58.6)	3.9 (4.1)	4.7[Cl] (3.8)
$[(PPh_3)_2Pd(CH_2SMe)SCN]$	$[(PPh_3)_2Pd(OCOCF_3)SCN]$	152–8	1680(CO) 2150(CN)	58.4 (58.1)	3.8 (2.8)	1.8[N] (2.2)
$[(PPh_2Me)_2Pd(CH_2SMe)Cl]$	$[(PPh_2Me)_2Pd(OCOCF_3)Cl]$	168–72	310(Pd–Cl) 1670(CO)	51.3 (50.6)	4.0 (4.1)	5.4[Cl] (5.1)
$[(PPh_2Me)_2Pd(CH_2SMe)Br]$	$[(PPh_2Me)_2Pd(OCOCF_3)Br]$	173–7	1670(CO)	48.1 (49.2)	3.7 (3.2)	11.4[Br] (12.7)
$[(PPh_2Me)_2Pd(CH_2SMe)I]$	$[(PPh_2Me)_2Pd(OCOCF_3)I]$	170–4 dec.	1670(CO)	45.0 (46.2)	3.5 (3.4)	17.0[I] (17.9)
$[(PPh_3)Pd(CH_2SMe)Cl]$	$[(PPh_3)Pd(OCOCF_3)Cl]_2$		260 310 (PdCl) 1675(CO)	46.5 (47.0)	2.9 (3.4)	6.9[Cl] (7.6)
$[(PPh_3)Pd(CH_2SMe)Br]$	$[(PPh_3)Pd(OCOCF_3)Br]_2$		1675(CO)	42.8 (43.0)	2.7 (3.3)	14.3[Br] (14.5)
$[(PPh_3)Pd(CH_2SMe)I]$	$[(PPh_3)Pd(OCOCF_3)I]_2$		1675(CO)	39.5 (39.0)	2.5 (2.8)	20.9[I] (21.6)

(continued on facing page)

TABLE III. *(continued)*

Organopalladium Reagent	Product	M.p. (°C)	ν (cm^{-1})	Analysis, Calc. (Found)			
				C	H	X	
With HCl							
$[(PPh_3)_2Pd(CH_2SPh)Cl]$	$[(PPh_3)_2PdCl_2]$	279–83 dec.	355(PdCl)	61.6 (60.3)	4.3 (4.3)	10.1[Cl] (11.1)	
$[(PPh_3)_2Pd(CH_2SPh)Br]$	$[(PPh_3)_2PdClBr]$	276–80 dec.	310(PdCl)	57.2 (57.7)	4.0 (4.0)	10.8[Br] (10.3)	4.9[Cl] (4.7)
$[(PPh_3)_2Pd(CH_2SPh)SCN]$	$[(PPh_3)_2PdCl_2]$	280–4 dec.	360(PdCl)	61.6 (61.2)	4.3 (4.3)	10.1[Cl] (9.8)	
$[(PPh_3)_2Pd(CH_2SPh)I]$	$[(PPh_3)_2PdClI]$	276–8 dec.	310(PdCl)	54.5 (52.0)	3.8 (3.5)	16.0[I] (18.2)[I]	4.8[Cl] (6.1)[Cl]
$[(PPh_3)_2Pd(CH_2SMe)Cl]$	$[(PPh_3)_2PdCl_2]$	280–82 dec.	355(PdCl)	61.6 (61.7)	4.3 (4.2)	10.1[Cl] (9.8)	
$[(PPh_3)_2Pd(CH_2SMe)SCN]$	$[(PPh_3)_2PdCl_2]$	278–282 dec.	360(PdCl)	61.6 (60.9)	4.3 (4.1)	10.1[Cl] (9.2)	
$[(PPh_2Me)_2Pd(CH_2SMe)Cl]$	$[(PPh_2Me)_2PdCl_2]$	190–2 dec.	310(PdCl) 290	54.1 (52.1)	4.5 (4.5)	12.3[Cl] (12.2)	
$[(PPh_2Me)_2Pd(CH_2SMe)Br]$	$[(PPh_2Me)_2PdClBr]$	189–94 dec.	300(PdCl)	50.2 (49.7)	4.2 (4.4)	13.1[Br] (12.9)[Br]	5.7[Cl] (6.2)[Cl]
$[(PPh_2Me)_2Pd(CH_2SMe)I]$	$[(PPh_2Me)_2PdClI]$	217–20 dec.				19.0[I] (22.1)[I]	5.3[Cl] (6.9)[Cl]
$[(PPh_3)Pd(CH_2SMe)Cl]$	$[(PPh_3)PdCl_2]_2$	260–6 dec.	360 300(PdCl) 270	49.2 (49.0)	3.4 (4.2)	16.2[Cl] (15.1)	
$[(PPh_3)Pd(CH_2SMe)Br]$	$[(PPh_3)PdClBr]_2$	256–62 dec.	360(PdCl)	44.7 (45.6)	3.4 (4.0)	16.6[Br] (17.5)	
$[(PPh_3)Pd(CH_2SMe)I]$	$[(PPh_3)PdClI]_2$	250–5 dec.	355(PdCl)	40.7 (41.1)	2.8 (3.4)	23.9[I] (23.6)	

(*a*) For all interactions of CH_3CO_2H and interactions involving low concentrations of CF_3CO_2H (*i.e.* up to 3 equivalents), addition of hexane to the $CDCl_3$ solution led to the recovery of the starting organopalladium compound in very high yield. Recrystallisation from dichloromethane/hexane gave products having analyses and physical properties in accord with the expected values.

(*b*) Solutions of the organopalladium compound and CF_3CO_2H (10 equivalents) in $CDCl_3$ were maintained at room temperature. The extents of protonolysis were monitored by g.l.c. At the completion of the reactions (about 2d for $[(PPh_2R)_2Pd(CH_2SR')X]$ and 7d for $[(PPh_3)Pd(CH_2SMe)X]$), addition of hexane resulted in the separation of oils or solids, which were crystallised from dichloromethane/hexane. Data for these compounds are in Table III.

Reactions with Hydrogen Chloride

(*a*) Hydrogen chloride was bubbled through a solution of the organopalladium compound (0.18–0.25 *M*) in $CDCl_3$. The solutions became paler in colour. An immediate change in $\delta(CH_2)$ occurred (see Table IV), and a yellow crystalline precipitate was collected; data for these products are listed in Table III.

(*b*) To a solution of $[(PPh_3)_2Pd(CH_2SPh)Cl]$ in $CDCl_3$ (0.28 *M*) was added successively equimolar MeOH and MeCOCl. The yellow solution immediately became paler in colour and $\delta(CH_2)$ changed from 2.42 to 2.96. Formation of PhSMe was monitored by ^1H NMR and g.l.c., with a 100% yield after 24 h. The yellow crystalline solid $[(PPh_3)_2PdCl_2]$ was collected by filtration; yield >95%.

Results and Discussion

Reactions of the complexes having monodentate CH_2SR' groups, as in $[(PPh_2R)_2Pd(CH_2SR')X]$ (R,R' = Me or Ph; X = Cl, Br, I or SCN), and bidentate groups, as in $[(PPh_3)Pd(CH_2SMe)X]$ (X = Cl, Br or I), were studied with the weak carboxylic acid, CH_3CO_2H, and with the strong acids, CF_3CO_2H and HCl.

Reactions of $[(PPh_2R)_2Pd(CH_2SR')X]$

Two stages of the proton acid/$[(PPh_2R)Pd(CH_2SR')X]$ interactions were recognised: (*a*) a reversible

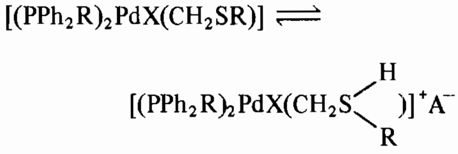
TABLE IV. Changes in ^{1}H δCH_2 on Addition of HCl to Solutions of [$(PPh_2R)_2Pd(CH_2SR')X$] in $CDCl_3$.

	[$(PPh_2R)_2Pd(CH_2SR')X$]	[$(PPh_2R)_2Pd(CH_2SR')$] + HCl
R = Ph, R′ = Ph, X = Cl	2.42	2.96
R = Ph, R′ = Ph, X = Br	2.73	2.96
R = Ph, R′ = Ph, X = SCN	2.47	3.29
R = Ph, R′ = Ph, X = I	2.96	2.96
R = Ph, R′ = Me, X = Cl	3.26	3.31
R = Ph, R′ = Me, X = SCN	3.13	3.28
R = Me, R′ = Me, X = Cl	2.71	2.82
R = Me, R′ = Me, X = Br	2.98	2.60
R = Me, R′ = Me, X = I	3.18	2.78

interaction using the weak acid CH_3CO_2H (all concentrations) or the stronger acid CF_3CO_2H, at low concentrations or with short reaction times, and (*b*) a irreversible reaction at higher concentrations and/or longer reaction times of CF_3CO_2H or with HCl (even one equivalent).

Additions of CH_3CO_2H or CF_3CO_2H (<3 equivalents) to the organopalladium compound in $CDCl_3$ solution led to changes in colour (orange to yellow) and in the ^{1}H NMR spectra, see Tables I and II. [Shifts in δCH_2 are also found on immediate addition of HCl, Table IV]. The NMR changes are most marked for complexes containing the CH_2SPh ligand; smaller changes are observed for the CH_2SMe complexes*. It is noteworthy that the values for δCH_2 obtained for the complexes in the presence of 2 equivalents of CF_3CO_2H are all 3.2 ± 0.1 (Table II), *i.e.* they cover a much smaller range of values than found for the organopalladium complexes in the absence of the acid (these are shown in Table IV). The reversible nature of this interaction is indicated by the recovery of the starting organopalladium compound on addition of hexane. The ^{1}H NMR spectrum and g.l.c. revealed that very little, if any, protonlysis of the complex to give MeSR′ had occurred under these conditions.

Our interpretation of this reversible reaction is protonation of the complex at sulphur to give (*III*)**. This requires a considerable enhancement of the basicity of the sulphur (arising from the α-Pd) as compared to that in simple organic sulphides. Protonation of sulphides, Me_2S or PhSMe, has been studied [5]. Such studies reveal that concentrated H_2SO_4 is required to effect protonation in aqueous media, much more powerful acid conditions than used in this study. Evidence for the enhanced basicity of S in the related platinum complex, [$(PPh_3)_2Pt(CH_2SMe)Cl$], has been found by Okawara *et al.* [6]. They showed that the sulphonium salt (*IV*) could be isolated from reaction with $MeOSO_2F$



$$[(PPh_2R)_2PdX(CH_2SR)] \rightleftharpoons [(PPh_2R)_2PdX(CH_2S\overset{H}{\underset{R}{<}})]^+A^-$$

(*III*)

$$[(PPh_3)_2PtCl(CH_2SMe)] + MeOSO_2F \longrightarrow [(PPh_3)_2PtCl(CH_2SMe_2)]^+SO_3F^-$$

(*IV*)

The irreversible reaction results when CF_3CO_2H (>3 equivalents) or HCl is used; the amounts of products of protonolysis increased with time:

$$[(PPh_2R)_2Pd(CH_2SR')X] + HA \xrightarrow{CHCl_3} [(PPh_2R)_2PdX(A)] + MeSR'$$

A = Cl or O_2CCF_3

Complete protonlysis of [$(PPh_3)_2Pd(CH_2SPh)X$] (X = Cl, Br, I or SCN) and [$(PPh_2R)_2Pd(CH_2SMe)X$] (R = Ph or Me; X = Cl or SCN) occurred using CF_3CO_2H (10 equivalents) in $CDCl_3$ solution within 2d; the SCN complexes were slightly the most reactive

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*Values of δCH_2SCH_3 also altered on addition of the acid.

**An alternative explanation for the shift in $\delta(CH_2)$ on addition of CH_3CO_2H or CF_3CO_2H to the organopalladium complex [$(PPh_2R)_2Pd(CH_2SR')X$] based on anion exchange, *i.e.* CR''_3CO_2 for X, can be dismissed as the only process in solution since shifts in $\delta(CH_2)$ result even for [$(PPh_3)_2Pd(CH_2SPh)Cl$] when HCl is added.

within each series. At the end of the reaction, as indicated by g.l.c. and NMR, hexane was added to precipitate the organopalladium reaction product (Table III). The products of reaction of CF_3CO_2H $[(PPh_2R)_2PdX(OCOCF_3)]$ (R = Me or Ph) had $\nu(CO)$ = 1670–1680 cm^{-1}, values expected for a monodentate CF_3CO_2 ligand. The products of reactions with HCl were dihalides $[(PPh_2R)_2PdXCl]$ (X = Cl, Br or I) or the $CHCl_3$ solvated species. Where mixed dihalides could be formed, analyses suggested that incompletely pure compounds were usually obtained after recrystallisation. The complexes isolated from the reactions of $[(PPh_2R)_2Pd(CH_2SPh)SCN]$ (R = Me or Ph) with HCl were $[(PPh_2R)_2PdCl_2]$.

The overall reaction with acids is considered to proceed *via* the protonated complex;

$$[(PPh_2R)_2Pd(CH_2SR')X] + HA \rightleftharpoons (III) \longrightarrow [(PPh_2R)_2PdX(A)] + MeSR'$$

Reactions of [(PPh₃)Pd(CH₂SMe)X]

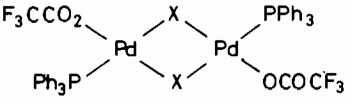
These compounds, containing the bidentate CH_2SMe group, react much less readily with proton acids in $CDCl_3$ solution than do the monodentate complexes. This points to a role in the protonolysis reaction for the sulphur since a coordinated sulphur, as in $[(PPh_3)PdCH_2SMe)X]$, is unable to act as a basic centre for the proton.

Addition of 2 equivalents of CF_3CO_2H resulted in only small changes in the ^1H NMR spectra (Table II). Reaction occurred when CF_3CO_2H (10 equivalents) or HCl (excess) were used:

$$[(PPh_3)Pd(CH_2SMe)X] \xrightarrow[CHCl_3]{HA} [(PPh_3)PdXCl]_2$$

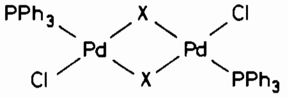
A = Cl or CF_3CO_2

The organopalladium products were isolated on addition of hexane and were recrystallised from dichloromethane/hexane. From the $[(PPh_3)Pd(CH_2SMe)Cl]$-CF_3CO_2H reaction, the product was $[(PPh_3)PdCl(O_2CCF_3)]_2$ (*V*, X = Cl). Details from its IR spectrum are $\nu(CO)$ at 1675 cm^{-1} (monodentate CF_3CO_2) and $\nu(PdCl)$ at 310 cm^{-1} (bridging and *trans*- to CF_3CO_2) and 260 cm^{-1} (bridging and *trans*- to PPh_3). Similar structures were envisaged for the other $[(PPh_3)PdX(OCOCF_3)]$ (X = Br or I) products.



(*V*)

The organopalladium complexes from the HCl/ $[(PPh_3)Pd(CH_2SMe)X]$ reactions were collected and recrystallised in a similar manner as were those from the CF_3CO_2H reactions. The product (*VI*) from reaction of $[(PPh_3)Pd(CH_2SMe)Cl]$ and HCl had IR absorptions at 360, 300 and 270 cm^{-1} corresponding to δ(PdCl) terminal, (bridging and *trans* to Cl) as well as (bridging and *trans*- to PPh_3 respectively [7]. Similar structures were assigned to all $[(PPh_3)PdXCL]_2$.



(*VI*)

X = Cl, Br or I

References

1 H. D. McPherson and J. L. Wardell, *Inorg. Chim. Acta, Submitted.*

2 G. Yoshida, Y. Matsumura and R. Okawara, *J. Organomet. Chem., 92,* C53 (1975);
G. Yoshida, H. Kurosawa and R. Okawara, *ibid., 113,* 85 (1976);
T. Chivas and P. L. Timms, *ibid., 118,* C37 (1976);
K. Miki, G. Yoshida, Y. Kai, N. Yasuaka and N. Kasai, *ibid., 149,* 195 (1978);
K. Miki, Y. Kai, N. Yasuaka and N. Kasai, *ibid., 165,* 79 (1979);
G. Yoshida, H. Kurosawa and R. Okawara, *Chem. Letts.,* 1387 (1977);
K. Miki, Y. Kai, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Jpn., 54,* 3639 (1981).

3 P. M. Maitlis, P. Espinet and M. J. H. Russell, in 'Comprehensive Organometallic Chemistry', Eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, 1982. Chapter 38.4.

4 H. D. McPherson and J. L. Wardell, *Inorg. Chim. Acta, 35,* L353 (1979).

5 P. Bonvicini, A. Levi, V. Lucchini and G. Scorrano, *J. Chem. Soc., Perkin Trans.,* 2267 (1972);
P. Bonvicini, A. Levi, V. Lucchini, G. Modena and G. Scorrano, *J. Am. Chem. Soc., 95,* 5966 (1973);
E. M. Arnett, *Prog. Phys. Org. Chem., 1,* 223 (1963).

6 G. Yoshida, H. Kurosawa and R. Okawara, *J. Organomet. Chem., 131,* 309 (1977).

7 R. J. Goodfellow, P. L. Goggin and L. M. Venanzi, *J. Chem. Soc. (A),* 1897 (1967).