Preparation of Mixed Dithio-β-diketonato (Tertiary Phosphine) Palladium(II) Complexes

MARTIN A. BENNETT
Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601 (Australia)
KINGSLEY J. CAVELL* and KOON Y. CHAN
Chemistry Department, University of Tasmania, Hobart, Tas. 7001 (Australia)
(Received January 23, 1989)

Abstract

Neutral and cationic palladium(II) dithio-β-diketonate complexes of general formula Pd{$CH_3C(S)CHC(S)CH_3$}X(L) and [Pd{$CH_3C(S)CHC(S)CH_3$}{(L-L′)}]Y (L = various monodentate tertiary phosphines; L-L′ = $Ph_2PCH_2CH_2PPh_2$, *o*-$CH_2 = CHC_6H_4PPh_2$; X = Br, I; Y = I, PF_6, BPh_4) are described. These are direct analogues of the nickel dithio-β-diketonate tertiary phosphine complexes which are precursors to highly active olefin oligomerization catalysts.

Introduction

Dithio-β-diketonate tertiary phosphine complexes of nickel(II) of general formulae Ni{$R^1C(S)CR^2C(S)R^3$}X(L) (**A**) and [Ni{$R^1C(S)CR^2C(S)R^3$}(L-L)]Y (**B**) [R^1, R^2, R^3 = alkyl or aryl, X = halide, Y = halide, BF_4, PF_6 etc.; L = various monodentate tertiary phosphines; L-L = various bidentate ditertiary phosphines] in the presence of an alkylaluminium compound form very active catalysts for the dimerization and oligomerization of propylene [1–4]. The catalysts exhibit versatility and flexibility in product selectivity and process design not encountered in other nickel-based catalysts such as those used in the Dimersol process and Shell's Higher Olefins Process [5–9].

Little is known about the active species in these systems or how they are formed during activation. The currently accepted mechanism for Ziegler systems of this type invokes a metal hydride as the active species [10]. Carbene intermediates similar to those involved in metallacycle-metathesis [11] and a metallocyclopentane intermediate [12] have also been suggested.

Approaches to delineating mechanisms normally involve kinetic studies, isolation or identification of intermediates, or model studies. The approach employed here is that based on model systems. Complexes containing similar ligands and displaying similar catalytic behaviour, i.e. requiring activation with a Lewis acid cocatalyst and showing activity for olefin isomerization and/or oligomerization, are required.

This paper is concerned with the preparation and characterization of pentane-2,4-dithionato (dithioacetylacetonato, $CH_3C(S)CHC(S)CH_3$, abbreviated SacSac) complexes of palladium(II), which are direct analogues of the nickel systems. The catalytic behaviour of the palladium systems in various olefin transformations and attempts to establish active intermediates in the nickel-based catalytic cycle will be described in later publications.

Experimental

Reagents

Manipulations were generally carried out under dry, oxygen free nitrogen in standard Schlenk apparatus. Transfers and additions of solutions, solvents etc. were made using cannulas and air-tight syringes. Solvents were dried and purified by standard methods and freshly distilled before use. Chemical reagents were used as received. Tertiary phosphines were purchased from Strem Chemicals and Aldrich Chemicals, or prepared by standard methods. Bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$] [13] and (2-vinylphenyl)diphenylphosphine(SP) [14] were prepared by literature methods. 3,5-Dimethyl-1,2-dithiolium iodide and bromide were prepared by a variation of the published method [15] in which the hydrogen sulphide cylinder was connected directly to the reaction vessel via a low pressure regulator to give a closed system. In this way an atmosphere of H_2S was maintained without the need to flow and hence dispose of excess reagent. Vigorous stirring was essential. This method also gave better yields. Bis(pentane-2,4-dithionato) palladium(II) [Pd-

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

$(SacSac)_2$] was prepared by treating $Pd(dba)_2$ with an appropriate mixture of the dithiolium iodide and sodium borohydride.

Measurements

Nuclear magnetic resonance (NMR) spectra were recorded at 22 °C on a Bruker AM-300 NMR spectrometer at 300.13 MHz (^1H), 75.48 MHz (^{13}C), and 121.50 MHz (^{31}P). The solvent was $CDCl_3$, unless otherwise stated. Chemical shifts (δ) are reported in ppm relative to internal $(CH_3)_4Si$ (^1H, ^{13}C), or to external 85% H_3PO_4 (^{31}P). Coupling constants (J) are given in Hz and NMR peaks are given as a singlet (s), doublet (d), triplet (t) and multiplet (m). Unlabelled NMR peaks can be assumed to be singlets. The vinyl protons of SP are numbered as shown in eqn. (3).

Infrared (IR) spectra were recorded in absorbance on a Digilab FTS 20E FT-IR Spectrophotometer. Potassium bromide disks (~2% wt./wt.) were used in the mid IR range (4000–500 cm^{-1}) and polyethylene disks (~10% wt./wt.) were used in the far IR range (500–140 cm^{-1}). Absorption bands (cm^{-1}) are described as strong (s), medium (m) or weak (w) in intensity.

Microanalyses were performed by the Canadian Microanalytical Services Ltd.

Syntheses of Complexes

General procedure

The general procedure for syntheses of **1** and **2** was as follows: $Pd(dba)_2$ was slurried in degassed, dry THF (30–50 ml) with constant stirring. After about 10 min, one equivalent of the dithiolium salt was added, followed, after *c.* 30 min by an equivalent amount of tertiary phosphine. Usually, the mixture then turned orange–red within several minutes.

Complexes **1** generally required purification by column chromatography. The crude product was dissolved in a minimum amount of dichloromethane (5–10 ml) and slurried with silica gel (1–2 g); the solvent was then removed by evaporation. The column was packed as a slurry with toluene as solvent. The dry silica gel with sample was then placed on the column and eluted with toluene. The first band was pink to red and contained mainly $Pd(SacSac)_2$. The second broad band was orange–red and contained the desired product. The eluant was then changed to 30:70 vol./vol. ether:toluene and a brownish band eluted which was found to be predominantly free dba.

*Iodo(pentane-2,4-dithionato)(triphenylphosphine)palladium(II) (**1a**)*

$Pd(dba)_2$ (1.15 g, 2.0 mmol), the dithiolium iodide (0.52 g, 2.0 mmol) and PPh_3 (0.53 g, 2.0 mmol) were mixed as described in the general procedure. The crude product was purified by column chromatography and recrystallized from ether to give **1a** as an orange–red solid (0.96 g, 77%). *Anal.* Found: C, 43.5; H, 3.6; S, 10.7. Calc. for $C_{23}H_{22}IPPdS_2$: C, 44.0; H, 3.6; S, 10.2%. ^1H NMR: dithioacetylacetonate: δ 2.27, 2.60 (CH_3); 7.22 (CH). PPh_3: δ 7.7(m); 7.45(m). ^{13}C NMR: dithioacetylacetonate: δ 33.35, 32.58 (methyl C); 185.10, 179.83 (quaternary C); 129.60 (methine C). ^{31}P NMR: δ 24.3 (free PPh_3 = –5.4).

*Bromo(pentane-2,4-dithionato)(triphenylphosphine)palladium(II) (**1b**)*

$Pd(dba)_2$ (0.28 g, 0.49 mmol) was slurried in 10 ml of THF and the mixture was cooled to 0 °C in an ice-bath. The dithiolium bromide (0.103 g, 0.51 mmol) and PPh_3 (0.137 g, 0.52 mmol) were added successively. The flask was allowed to reach room temperature gradually and stirring was continued overnight. The mixture was then filtered and the filtrate was evaporated to 5 ml to precipitate the product as an orange solid. Further crystallization from the filtrate yielded more orange solid. The total yield of **1b** was 0.13 g (46%). *Anal.* Found: C, 48.8; H, 4.2; S, 11.1. Calc. for $C_{23}H_{22}BrPPdS_2$: C, 47.6; H, 3.8; S, 11.1%. ^1H NMR: dithioacetylacetonate: δ 2.29, 2.58 (CH_3); 7.21 (CH). PPh_3: δ 7.7(m); 7.5(m).

*Iodo(pentane-2,4-dithionato){2-vinylphenyl)diphenylphosphine}palladium(II) (**1c**)*

$Pd(dba)_2$ (0.58 g, 1.0 mmol), the dithiolium iodide (0.26 g, 1.0 mmol) and SP (0.29 g, 1.0 mmol) were allowed to react as described in the general procedure. The crude product was purified by column chromatography and recrystallized from ether to give **1c** as an orange solid (0.50 g, 77%). *Anal.* Found: C, 45.9; H, 3.7; S, 10.0. Calc. for $C_{25}H_{24}IPPdS_2$: C, 46.0; H, 3.7; S, 9.8%. ^1H NMR: dithioacetylacetonate: δ 2.59, 2.30 (CH_3); 7.21 (CH). SP: δ 5.54 (dd, H^3) (J_{13} 16.2 Hz, J_{23} 0.7 Hz), 5.06 (dd, H^2) (J_{12} 10.8 Hz) 7.7 (m, Ph), 7.4 (m, Ph). ^{13}C NMR: dithioacetylacetonate: δ 33.21, 32.67 (methyl C); 184.64, 179.99 (quaternary C). SP: δ 116.98 (CH_2). ^{31}P NMR: δ 19.8 (free SP = –13.8).

*Iodo(pentane-2,4-dithionato)(tri-n-butylphosphine)palladium(II) (**1d**)*

A mixture of $Pd(dba)_2$ (0.56 g, 0.97 mmol), the dithiolium iodide (0.26 g, 1.0 mmol) and PBu_3 (0.20 g, 0.99 mmol) in THF was set aside overnight and the mixture was then evaporated to dryness. The crude product was extracted first with petroleum ether (40 ml) by stirring for several hours at room temperature and then again with hot petroleum ether. Both extracts were combined and purified by column chromatography. The second band gave an orange oil which was stirred with petroleum ether (about 1 ml) and cooled to –20 °C overnight to give **1d** as an orange–red solid (0.20 g, 36%). *Anal.* Found: C,

36.1; H, 6.1; S, 12.2. Calc. for $C_{17}H_{34}IPPdS_2$: C, 36.0; H, 6.1; S, 11.3%. ^1H NMR: dithioacetylacetonate: δ 2.57, 2.51 (CH_3); 7.31 (CH). PBu_3: δ 2.15(m), 1.43(m) ($P\text{-}CH_2CH_2CH_2$); 0.91(t) (CH_3). ^{13}C NMR: dithioacetylacetonate: δ 34.17, 33.10 (methyl C); 186.73, 177.70 (quaternary C); 130.86 (methine C).

Iodo(pentane-2,4-dithionato)(tricyclohexylphosphine)palladium(II) (1f)

$Pd(dba)_2$ (0.58 g, 1.0 mmol), dithiolium iodide (0.26 g, 1.0 mmol) and PCy_3 (0.28 g, 1.0 mmol) were allowed to react as described in the general procedure. The crude product was purified by column chromatography and recrystallized from ether to give **1f** as an orange solid (0.35 g, 55%). ^1H NMR: dithioacetylacetonate: δ 2.54, 2.48 (CH_3); 7.25 (CH). ^{13}C NMR: dithioacetylacetonate: δ 33.98, 33.07 (methyl C); 185.63, 129.77 (methine C). ^{31}P NMR: δ 31.5 (fee PCy_3 = 11.3).

Attempted synthesis of chloro(pentane-2,4-dithionato)(triphenylphosphine)palladium(II) by comproportionation

$Pd(SacSac)_2$ (0.109 g, 0.3 mmol) was refluxed with $PdCl_2(PPh_3)_2$ (0.214 g, 0.31 mmol), in benzene for 3 h. The ^1H NMR spectrum of the crude product gave dithioacetylacetonate CH_3 chemical shifts at δ 2.58 ppm and 2.30 ppm and the IR spectrum indicated that the desired complex was present. However the yield was low and further work is required to optimize the reaction conditions.

(Pentane-2,4-dithionato){2-vinylphenyl)diphenylphosphine}palladium(II) hexafluorophosphate

Complex **1b** (0.111 g, 0.17 mmol) was dissolved in about 20 ml of THF. When an excess of $TlPF_6$ was added an orange–brown precipitate formed immediately. The reaction mixture was stirred overnight. The mixture was evaporated to dryness and dissolved in a few ml of dichloromethane. The yellow residue was predominantly TlI. The filtrate was evaporated to about 2 ml and ether was added to give a yellow–brown solid, $[Pd(SacSac)(SP)]PF_6$ (0.090 g, 79%). ^1H NMR: dithioacetylacetonate: δ 2.85, 2.62 (CH_3). SP: δ 5.98 (dd, H_2) J_{12} 8.7 Hz, 4.93 (dd, H^3) J_{13} 15.9 Hz, J_{23} or J_{PH} 3.3 Hz. ^{13}C NMR: dithioacetylacetonate: δ 33.96, 32.35 (methyl C); 189.98, 181.12 (quaternary C). SP: δ 94.34 (CH_2).

(Pentane-2,4-dithionato){bis(diphenylphosphino)ethane}palladium(II) iodide (2a)

$Pd(dba)_2$ (0.56 g, 0.97 mmol) was dissolved in 30 ml of THF. The dithiolium iodide (0.26 g, 1.0 mmol) and dppe (0.40 g, 1.0 mmol) were added successively to the solution. After 1 h, a fine precipitate was obtained. The mixture was filtered and the product was washed with THF (2 × 20 ml) and ether (2 × 20 ml). The crude product was recrystallized from methanol to give **2a** as a yellow solid (0.48 g, 65%). *Anal.* Found: C, 47.5; H, 4.1; S, 9.7. Calc. for $C_{31}H_{31}IP_2PdS_2$: C, 48.8; H, 4.1; S, 8.4%. ^1H NMR: dithioacetylacetonate: δ 2.63 (CH_3). dppe: δ 3.10 (d) J 22.6 Hz. ^{13}C NMR: dithioacetylacetonate: δ 35.06 (methyl C); 190.09 (quaternary C); 133.12 (methine C). ^{31}P NMR: δ 56.5 (free dppe = −12.6).

(Pentane-2,4-dithionato){bis(diphenylphosphino)ethane}palladium(II) hexafluorophosphate (2b)

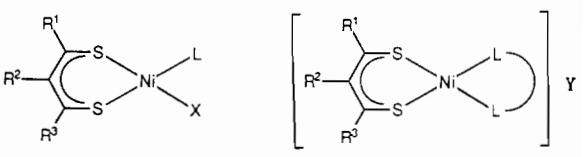
Complex **2a** (0.092 g, 0.13 mmol) was dissolved in 1 ml of methanol and treated with an excess of $TlPF_6$. The precipitated TlI was removed by filtration. The product crystallized on addition of petroleum ether as a microcrystalline yellow solid (0.078 g, 77%). *Anal.* Found: C, 46.4; H, 3.9; S, 9.1. Calc. for $C_{31}H_{31}F_6P_3PdS_2$: C, 47.6; H, 4.0; S, 10.2%. ^1H NMR: dithioacetylacetonate: δ 2.63 (CH_3). dppe: δ 2.89 (d) J 22.5 Hz.

(Pentane-2,4-dithionato){bis(diphenylphosphino)ethane}palladium(II) tetraphenylborate (2c)

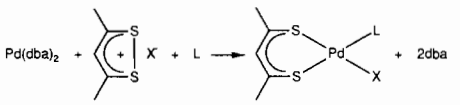
Complex **2a** (0.089 g, 0.12 mmol) was dissolved in 1 ml of methanol. An excess of $NaBPh_4$, dissolved in 2 ml of methanol, was added. Immediately a bright yellow precipitate was obtained. The precipitate was collected, dissolved in the minimum amount of dichloromethane, and crystallized by addition of ether to give **2c** as a microcrystalline yellow solid (0.106 g, 95%). *Anal.* Found: C, 67.7; H, 5.5; S, 6.9. Calc. for $C_{55}H_{51}BP_2PdS_2$: C, 69.1; H, 5.4; S, 6.7%. ^1H NMR: dithioacetylacetonate: δ 2.57 (CH_3). dppe: δ 2.07(d) J 23.1 Hz. ^{31}P NMR: δ 57.5 (free dppe = −12.6).

Results and Discussion

Palladium analogues **1** and **2a** of the nickel complexes **A** and **B** have been prepared by oxidative addition of 3,5-dimethyl-1,2-dithiolium bromide or iodide to the zerovalent palladium complex bis(dibenzylideneacetone)palladium(0), $Pd(dba)_2$, in the presence of the appropriate tertiary phosphine (L) (eqns. (1) and (2)). The yields of **1** were 50–80% for triphenylphosphine (PPh_3) and (2-vinylphenyl)diphenylphosphine ($o\text{-}CH_2{=}CHC_6H_4PPh_2$, sometimes called *o*-styryldiphenylphosphine, and

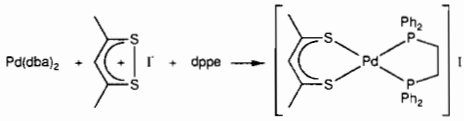


A **B**



(1)

1



(2)

2a

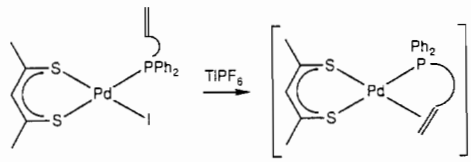
Complex	X	L
1a	I	PPh_3
1b	Br	PPh_3
1c	I	SP
1d	I	PBu_3
1e	I	PBu_3
1f	I	PCy_3

abbreviated SP), and 35–50% for tricyclohexylphosphine (PCy_3) and tri-n-butylphosphine (PBu_3). The tri-t-butylphosphine complex was obtained in poor yield, however enough sample was obtained for spectroscopic characterization. ^{1}H NMR: dithioacetylacetonate: δ 2.52, 2.58 (CH_3); 7.33 (CH). ^{13}C NMR: dithioacetylacetonate: δ 34.70, 33.08 (methyl C); 185.78, 176.41 (quaternary C); 129.56 (methine C).

The liberated dibenzylideneacetone (dba) is soluble to some extent in most organic solvents and it was the major impurity associated with the complexes **1**. Recrystallization was not effective in its removal. However, the complexes **1** can be purified by column chromatography on silica gel with toluene as eluant; this serves to remove both dba and Pd(SacSac)$_2$, which is formed in variable amounts as a by-product. This procedure is unnecessary in the case of **2a**, which precipitates from solution in high yield, and can be purified by recrystallization. **2a** can be converted into the corresponding PF_6 or BPh_4 salts (**2b**, **2c**) by treatment with $TlPF_6$ or $NaBPh_4$.

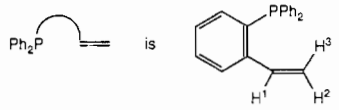
In agreement with the proposed structure, the ^{1}H NMR spectra of **1** show two singlets between δ 2–3 ppm due to inequivalent methyl groups of SacSac, in addition to a singlet at δ *c.* 7 ppm due to the γ-proton and resonances arising from the tertiary phosphine. Correspondingly, the ^{13}C NMR spectra of **1** show two signals at δ c. 33 ppm due to the inequivalent quaternary carbon atoms, and a single resonance at δ *c.* 130 ppm due to the methine carbon atom. In contrast, the ^{1}H NMR spectra of the nickel analogues of **1** at room temperature show a singlet for the SacSac methyl protons. A rapid intermolecular exchange of halide has been proposed to explain this observation [16]. The methyl resonances of Pd(SacSac)Br(PPh_3) (**1b**) did not change even at 105 °C in toluene-d_8, showing that the halide ligand is, as expected, more tightly bound to palladium(II) than to nickel(II).

The ^{1}H NMR spectrum of Pd(SacSac)I(SP) (**1c**) shows a pair of doublets at δ 5.54 ppm (J_{13} 16 Hz) and δ 5.06 ppm (J_{12} 11 Hz) which are due to the β-vinyl protons H^3 and H^2 respectively of the SP ligand; the resonance due to the α-proton H^1 is masked by the aromatic resonances. The chemical shifts and coupling constants are close to those of free SP, confirming that in **1c** the vinyl group is not bound to the metal. In the ^{1}H NMR spectrum of the PF_6 salt (**3**) formed by treatment of **1c** with $TlPF_6$ (eqn. (3)) the resonance due to H^2 (δ 5.98 ppm, J_{12}



(3)

1c 3



8.6 Hz) is less shielded than that due to H^3 (δ 4.93 ppm, *J* 15.9 Hz). This indicates that the vinyl group in the PF_6 salt is coordinated to the metal, H^3 having been shielded by *c.* 0.6 ppm and H^2 being slightly deshielded relative to the free ligand. The relatively small changes in chemical shift and coupling constant suggest that the olefin is only slightly perturbed on coordination to palladium(II) in complex **3**. A similar conclusion was reached in the case of the palladium(II) salt *trans*-[Pd{*o*-$CHMeC_6H_4PPh_2$}(SP)]BF_4 formed by protonation of Pd(SP)$_2$ [17].

The IR spectra of the complexes in the region 400–150 cm^{-1} are collected in Table 1. Weak bands in the region of 320–400 cm^{-1} seem to be characteristic of coordinated SacSac and some may be due to Pd–S stretching vibrations. Complexes **1a**–**1d** show weak or medium intensity bands at *c.* 250 and *c.* 160 cm^{-1} that may be due to Pd–Br and Pd–P stretching, cf. *trans*-$PdBr_2(PPh_3)_2$ 286 cm^{-1} [ν(Pd–

TABLE 1. Far IR spectra of palladium(II) complexes

1a	**1b**	**1c**	**1d**	**2a**	**2b**	**2c**
399(w)	371(w)	399(w)	390(w)	389(m)	389(m)	388(w)
365(w)	350(w)	366(w)	366(w)	365(w)	358(s)	354(w)
347(w)			352(w)	351(m)	328(w)	348(w)
				328(w)		327(w)
278(w)	275(w)	267(w)	268(w)	267(w)	291(w)	287(w)
270(w)	254(w)	249(w)	249(m)	255(w)	266(w)	256(w)
253(w)		241(w)		237(w)	254(w)	
228(w)					233(w)	
155(m)	162(m)	153(m)	156(m)			

Br)] and 150 cm^{-1} [ν(Pd–P)] [18], but definite assignments cannot be made at present.

The complex Pd(SacSac)Br(PPh_3) is formed to some extent on heating $Pd(SacSac)_2$ and $PdBr_2(PPh_3)_2$ in benzene, but the reaction clearly occurs less readily than the corresponding comproportionation between $NiX_2(PR_3)_2$ and $Ni(SacSac)_2$ [1]. Thus the oxidative addition of 3,5-dimethyl-1,2-dithiolium bromide or iodide to a palladium(0) complex in the presence of a tertiary phosphine provides a convenient route to the mixed ligand complexes Pd(SacSac)X(L). The key step is the transfer of two electrons from Pd(0) to the dithiolium ion, which breaks the S–S bond and generates the pentane-2,4-dithionate anion coordinated to Pd(II); simultaneous or subsequent coordination of halide and of tertiary phosphine completes the process. Free 3,4-diaryldithiolium cations undergo an electrochemical two-electron reduction similar to the metal-based reduction described here [19]. Reductive cleavage of the S–S bond in diaryl disulphides has been used to prepare arylthiolato complexes of nickel(II) from nickel(0) carbonyls [20].

Acknowledgements

The authors thank Drs M. Ridd and I. Burger, Central Science Laboratory, University of Tasmania, for FT-IR and NMR measurements, respectively. Research support was provided by ARGS and Special University of Tasmania Grants.

References

1 K. J. Cavell and A. F. Masters, *J. Chem. Res.*, (1983) 72.
2 *US Pat 4533651* to CSIRO, K. J. Cavell and A. F. Masters.
3 K. J. Cavell and A. F. Masters, *Aust. J. Chem., 39* (1986) 1129.
4 K. J. Cavell, in D. M. Bibby, C. D. Chang, R. F. Howe and S. Yurchak (eds.), *Studies in Surface Science and Catalysis*, Vol. 36, Elsevier, Amsterdam, 1988, p. 523.
5 Y. Chauvin, J. F. Gaillard, D. V. Quang and J. W. Andrews, *Chem. Ind. (London)*, (1974) 375.
6 J. W. Andrews and P. L. Bonifay, *Hydrocarbon Process.*, (1977) 161.
7 M. Sherwood, *Chem. Ind. (London)*, (1982) 994.
8 E. R. Freitas and C. R. Gum, *Chem. Eng. Prog.*, (1979) 73.
9 E. F. Lutz, *J. Chem. Educ., 63* (1986) 202.
10 B. Bogdanović, *Adv. Organomet. Chem., 17* (1979) 105.
11 K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green and R. Mahtab, *J. Chem. Soc., Chem. Commun.*, (1978) 604.
12 P. W. Jolly, in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 8, Pergamon, Oxford, 1982, Vol. 8, Ch. 56.2.
13 M. F. Rettig and P. M. Maitlis, *Inorg. Synth., 17* (1977) 134.
14 M. A. Bennett, R. S. Nyholm and J. D. Saxby, *J. Organomet. Chem., 26* (1971) 293.
15 A. R. Hendrickson and R. L. Martin, *J. Org. Chem., 38* (1973) 2548.
16 M. A. Bennett, K. J. Cavell and A. F. Masters, in preparation.
17 M. A. Bennett, C. Chiraratvatana, G. B. Robertson and U. Tooptakong, *Organometallics, 7* (1988) 1403.
18 K. Shobatake and K. Nakamoto, *J. Am. Chem. Soc., 92* (1970) 3332.
19 K. Bechgaard, V. D. Parker and C. Th. Pedersen, *J. Am. Chem. Soc., 95* (1973) 4373.
20 R. G. Hayter and F. S. Humiec, *J. Inorg. Nucl. Chem., 26* (1964) 807.