Journal of Organometallic Chemistry, 415 (1991) 259–268
Elsevier Sequoia S.A., Lausanne
JOM 22112

Synthesis of σ-alkyl diketonato and monothio β-diketonato complexes of platinum(II) and palladium(II)

Hong Jin and Kingsley J. Cavell *
Chemistry Department, University of Tasmania, Hobart, Tasmania 7001 (Australia)

(Received April 18th, 1991)

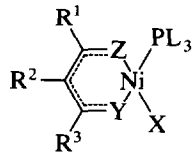
Abstract

A variety of Pt^{II} and Pd^{II} σ-methyl complexes of general formula $MMe(\beta\text{-dik})(PPh_3)$ (M = Pt, Pd; β-dik = β-diketonate or monothio-β-diketonate ligands) have been prepared and fully characterized. The structures of the complexes are very sensitive to the nature of the β-dik ligand, both in terms of the coordinating atoms (*O,O* or *O,S*) and with respect to the moieties attached to the backbone of the β-dik ligand. In complexes containing the monothio-β-diketonate ligand the σ-methyl ligand always selects a coordination site that is predominantly *trans* to the oxygen atom.

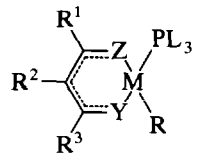
Introduction

The β-diketonate type ligands $R^1C(O)CR^2C(O)R^3$ (acac) and $R^1C(X)CR^2C(Y)R^3$ (X = S, Y = O, *sacac*; X = Y = S; *sacsac*) play important roles in the formation of various transition metal based catalyst species [1–8]. The considerable versatility and very high activity of many of these catalyst systems containing β-diketonate type ligands warrants further investigation, and if further development of these catalysts is to take place then an understanding of the influence of the ligand on the important catalytic steps is essential. We are engaged in a series of modelling studies aimed at delineating the role of the chelating ligand in the active catalytic system. In general the active species is formed by reacting the precursor complex **A** with an alkyl aluminium cocatalyst. In our studies we have assumed that the major role of the alkyl aluminium chloride cocatalyst is to alkylate the transition metal centre and that the chelating ligand remains firmly attached to the resulting active centre. We feel that the resulting alkylated complex plays an important role in the catalytic cycle. Here we describe the preparation and characterization of a series of mixed ligand alkyl complexes of type **B**, where R = Me and L = Ph, and a study of the influence of the chelating ligand on the structure complex.

0022-328X/91/$03.50



(A) Z = Y = O, S
Z = O; Y = S
X = Cl, Br, I



(B) M = Pt or Pd
Z = Y = O
Z = O, Y = S
R = alkyl or aryl group

Results and discussion

1. Preparation of methyl(β-dik)(triphenylphosphine)platinum(II) and palladium(II) complexes *

Sodium β-diketonates and sodium monothio-β-diketonates, except 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, readily react with $PtMe(THF)_x(PPh_3)_2$ (**3**), which is generated *in situ* from *trans*-$PtMeI(PPh_3)_2$ (**1**) and $TlPF_6$ in THF at room temperature, to yield the *O,O*-chelated β-dik complexes $PtMe(\beta\text{-dik})(PPh_3)$ (**4–6**) and *O,S*-chelated monothio-β-dik complexes $PtMe(\beta\text{-O,S-dik})(PPh_3)$ (**10,11**). The palladium(II) analogues of these complexes, i.e. **7–9**, **12** and **13**), were made in a similar manner from *trans*-$PdMeI(PPh_3)_2$ (**2**) (Scheme 1). Unfortunately attempts to prepare *S,S*-chelated dithio-β-dik complexes of the type $MR(\beta\text{-}S,S\text{-dik})PL_3$ have been unsuccessful at this stage.

$PtMe(Ph\text{-}sacac)(PPh_3)$ (**10**) and $PdMe(Ph\text{-}sacac)(PPh_3)$ (**12**) were also prepared by reacting **1** or **2** with thallium(I) (Ph-sacac) in THF. It is likely that a large selection of similar complexes could be obtained by this route [9].

In the case of the reaction with hfac anion which is the least basic β-dik ligand employed, the complex $PtMe(\beta\text{-hfac})(PPh_3)$ could not be obtained by any route mentioned above. This is presumably because of the inability of the hfac anion to displace coordinated PPh_3.

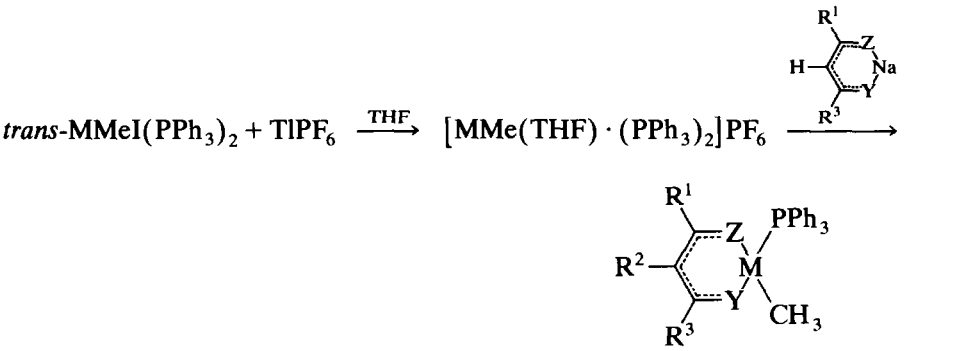
All the reactions are summarized in Scheme 1. Spectroscopic data for these newly prepared complexes are listed in Tables 1 to 4.

2. Characterization of the chelated β-dik complexes

IR spectra of all complexes exhibit bands of strong to medium intensities in the 1620–1500 cm^{-1} region, which are assigned to the $\nu(C\cdots O) + \nu(C\cdots C)$ vibrations of the *O,O*-chelated or monothio *O,S*-chelated β-dik ligands [10].

Table 1 lists the ^1H NMR data for the acac complexes in $CDCl_3$. The spectra of the complexes are relatively simple. The platinum complexes exhibit singlets at δ 1.6–1.8 and at 1.9–2.1. The former are assigned to the methine proton of the β-dik ligand which are *cis* to P and the latter are assigned to the methyl protons *trans* to P [11,12]. A singlet at δ 5.3–5.7 is due to the methine proton of the β-dik ligand. A

* In this paper β-dik represents a β-diketones such as 2,4-pentanedione(acaH) 1,1,1-trifluoro-2,4-pentanedione(tfacH), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione(hfacH), 1-benzoylacetone[Ph-acacH]; or monothio-β-diketones, such as 3-mercapto-1-phenylbut-2-en-1-one(Ph-sacsac), 4-mercaptopent-3-en-2-one.



M = Pt or (Pd); R^2 = H

4(7): $R^1 = R^3$ = Me, Z = Y = O;

5(8): R^1,R^3 = Me or CF_3, Z = Y = O;

6(9): R^1,R^3 = Me or Ph, Z = Y = O;

10(12): R^1 = Ph, R^3 = Me, Z = O, Y = S

11(13): $R^1 = R^3$ = Me, Z = O, Y = S;

Scheme 2. Preparation of α-methyl β-dik type complexes of Pt(II) and Pd(II).

doublet at δ 0.6–0.9 is assigned to the Pt-methyl protons coupled to *cis* ^{31}P, the observed coupling constants being appropriate for *cis* coupling [13]. This doublet is flanked by ^{195}Pt satellites with coupling constants as expected for platinum(II) methyl complexes [14]. In addition at δ 6.5–7.5 there are signals assignable to the phenyl protons.

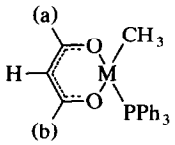
The chemical shifts of the corresponding protons in the palladium complexes are similar to those of the related platinum complexes, as shown in Table 1.

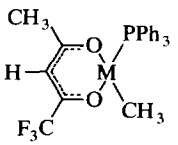
The $^{31}P\{^1H\}$ NMR spectrum of **4** (Table 3) in C_6D_6 shows a singlet at δ 9.8 with satellite bands due to ^{195}Pt. The analogous Pd complex, **7**, shows the ^{31}P resonance at δ 36.6. The coupling constant, $^1J(^{195}Pt-^{31}P)$, of 4909 Hz for **4** does not differ greatly from reported values of 4490 Hz for Pt(acac)(r-acac)(PPh_3) [15], but it is much greater than the complexes with a hydroxo or alkoxo anion ligand [16–18]. This may be a consequence of the slightly greater *trans* influence of the oxygen atom in a conjugated acac ligand compared with the hydroxo and alkoxo ligands.

The $^{13}C\{^1H\}$ NMR spectrum of **4**, as shown in Table 4, in CCl_3 has a doublet at δ −18(J(PC) = 3 Hz) with ^{195}Pt satellites (^1J(PtC) = 726 Hz) due to Pt–CH_3. The methine carbon of the acac ligand was located at δ 102 as a singlet flanked with ^{195}Pt satellites (^2J(PtC) = 60 Hz). Carbon signals due to the acac ligand in **4** (Table 4) are almost unchanged from those of $Pd(acac)_2$ [15] and their chemical shifts are very similar to those reported for Pt(acac)(r-acac)(PPh_3) [15]. When unsymmetrically substituted β-diketonate ligands are used, two regioisomeric complexes are expected. Indeed, the spectrum of PtMe(tfac)(PPh_3) (**5**) in $CDCl_3$ is rather complex and shows two Pt-CH_3 signals at δ 0.74 and 0.76, and two methyl signals for the acac ligand at δ 1.7 and 2.1 in the intensity ratio of ca. 2:1. By reference to

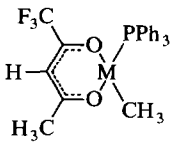
Table 1

^{1}H NMR data for the *O,O*-chelated β-dik complexes in $CDCl_3$





cis-(Me, P)



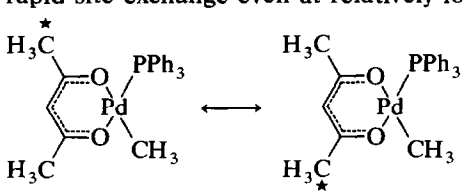
trans-(Me, P)

Entry	*cis*/*trans* Ratio	Isomers	β-dik			CH_3 (J(PH)/J(PtH)
			CH_3 (a)	CH_3 (b)	CH	
M = Pt						
4		–	1.63	1.97	5.3	0.65 d (3.0/75)
5	1/2	**5a**-*cis*	1.7	CF_3	5.7	0.74 d (2.4/77)
		5b-*trans*	CF_3	2.1		0.76 d (2.2/77)
6	1/2	**6a**-*cis*	2.2	C_6H_5	6.2	0.86 d (2.4/75)
		6b-*trans*	C_6H_6	1.9		0.91 d (2.4/72)
M = Pd						
7		–	1.7	2.0	5.3	0.56 d (2.0)
8	1/1	**7a**-*cis*	1.8	CF_3	5.7	0.69 d (2.0)
		7b-*trans*	CF_3	2.1		0.70 d (2.0)
9	1/2	**9a**-*cis*	2.4	C_6H_5	6.1	0.77 d (3.0)
		9b-*trans*	C_6H_5	2.3		0.82 d (3.0)

the data of PtMe(acac)(PPh_3) (**4**), these two sets of signals are readily attributed to the *cis* and *trans* isomers **5a** and **5b**.

Similar observations were made for the palladium(II) analogues **8** and **9**.

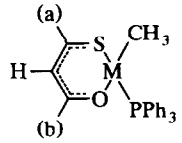
In a variable temperature ^{1}H NMR experiment, two singlets at δ 1.6 and 1.9 due to the two methyl groups of the acac ligand in PdMe(acac)(PPh_3) (**7**) broaden and the sharp doublet at δ 0.98 (^3J(PH) = 2 Hz) due to the σ-methyl resonance in **7** becomes a sharp singlet as the temperature is raised to 90 °C. These changes in the spectrum may be interpreted by assuming that acceleration in the dissociation and recombination of the phosphine ligand [19] or the acac ligand occurs at higher temperature thus accelerating the exchange rate between (a) and (b) below. In contrast, the nickel analogous NiMe(acac)(PPh_3) and NiEt(acac)(PPh_3) undergo rapid site exchange even at relatively low temperatures [20,21].

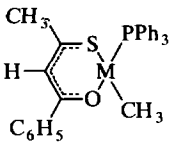


(a) (b)

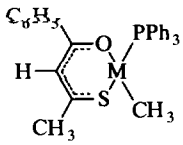
Table 2

^{1}H NMR data for the *O,S*-chelated β-dik complexes in $CDCl_3$





cis-(S, P)



trans-(S, P)

Entry	*cis* / *trans* Ratio	Isomers	β-dik		CH_3 (J(PH)/J(PtH))
			CH_3 (a)	CH_3 (b)	
M = Pt					
10	1/5	**10a**-*cis*	2.4	C_6H_5	0.62 d (2.4/57)
		10b-*trans*	2.2	C_6H_5	0.52 d (6.0/83)
11		*trans* only	1.6	2.2	0.47 d (5.0/83)
M = Pd					
12		*trans* only	2.6	C_6H_5	0.40 d (3.0)
13		*trans* only	2.4	1.8	0.34 d (2.0)

When the monothio *O,S*-β-dik ligand Ph-sacac was used, two geometrical isomers *cis*-(*S,P*) and *trans*-(*S,P*) complexes were expected (Table 2).

The NMR spectra of the products of the reaction indicate that both isomers are formed, with one isomer predominating. From the ^{31}P{^{1}H} NMR spectrum of **10**

Table 3

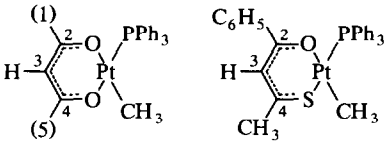
^{31}P{^{1}H} NMR spectral data for the β-dik complexes [a]

No.	Isomers	δ(P) [a]	^1J(Pt–P) (Hz)
4		9.8	4909
5	**5a**	8.8	4949
	5b	7.4	5011
6	**6a**	11.9	4848
	6b	10.5	4836
7		36.6	
8	**8a**	37.3	
	8b	36.4	
9	**9a**	37.6	
	9b	36.7	
10	**10a**	13.5	4740
	10b	21.2	3723
11		21.0	3713
12		27.3 [b]	
13		28.1	

[a] Measured in C_6D_6. [b] Measured in $CDCl_3$.

Table 4

Selected $^{13}C\{^1H\}$ NMR data for some of the β-dik type platinum(II) complexes in $CDCl_3$



(10b)

No.	Isomer	Acac					CH_3 (J(PC)/J(PtC))
		C^1	C^5	C^2	C^4	C^3	
3		27.9 s	27.5 d (3 Hz)	184 s	186 s	102 s (J(PtC) = 60)	−18.0 d (3.0/726 Hz)
4	*cis*-**4**	28.3 s	CF_3	[a]	[a]	96.7 s (J(PtC) = 60)	−16.6 d (6.0/723 Hz)
	trans-**4**	CF_3	28.9 d (8 Hz)			97.1 s (J(PtC) = 56)	−17.5 d (6.0/723 Hz)
10b			34.3 d (9 Hz)	179 s	176 s	118 s (J(PtC) = 53)	−23.2 d (7.6/705 Hz)

[a] Not observed.

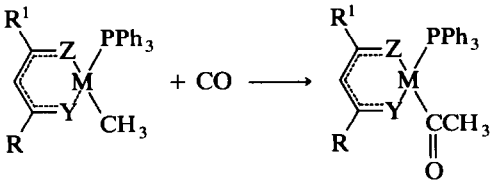
(Table 3), the two isomers may be identified. The major peak appearing at δ 21.2 with ^{195}Pt satellites (^1J(PtP) = 3723 Hz) is due to the major isomer **10b**. The coupling constant for this isomer, by comparison with the literature, indicates that the phosphorus atom is *trans* to a sulphur atom [18,22,23]. The other signal appearing at δ 13.5 with $^{195}Pt-^{31}P$ coupling of 4740 Hz, is attributed to the *cis*-(*S*,*P*) structure **10a**.

In keeping with these results, two sets of resonances are also observed in the ^1H NMR spectrum of PtMe(Ph-sacac)(PPh_3) (**10**) in $CDCl_3$ as shown in Table 2. The relative ratio of the two complexes (**10a** : **10b** is ca. 1 : 5. The magnitude of J(PtH) (83 Hz) in **10b** is consistent with the assignment that the σ-methyl group in **10** is *trans* to an O atom. The methine signal in the monothio-β-dik complexes could not be observed and is probably masked by the multiple resonances of the PPh_3 ligands [24,25].

Only one set of resonances due to the predominant isomer **10b**, is observed in the $^{13}C\{^1H\}$ NMR spectrum of **10** (Table 4). This is attributed to the low concentration of the minority isomer **10a**. The long-distance coupling of $^{31}P-^{13}C$ (9 Hz) again indicates the σ-methyl group in the major isomer **10b** is *trans* to PPh_3 [9]. Only one regio-isomer, i.e. the analogue of **10b**, is observed in the corresponding palladium(II) complex PdMe(Ph-sacac)(PPh_3) (**12**).

Interestingly, complexes containing the monothio *O*,*S*-β-dik ligand sacac (i.e. with CH_3-groups in the 2 and 4 positions) only occur in one isomeric form, i.e. where S is *trans* to P. This configuration is strongly preferred and it is only in the substituted monothio-β-dik ligand (Ph-sacac) that some of the *cis* form occurs. Whether the Ph-group exerts a predominantly steric or electronic influence on the structure is unclear at this stage. However as the Ph-group is well removed from the metal centre and considering that the cis isomer occurs only in the case of the platinum complex and not for palladium, purely steric control appears unlikely.

Preliminary studies with CO indicate that the β-dik complexes readily insert CO at room temperature to form the corresponding acyl complexes.



The palladium acyl complexes slowly decompose to deposit palladium metal. In contrast, the platinum acyl complexes appear quite stable. Details of the reaction of the β-dik complexes with CO and the mechanism of the insertion process are still under investigation and will appear in a forthcoming publication. A series of σ-aryl β-dik type complexes have also been prepared and their reactions with CO studied. Results from these studies will be reported shortly.

Experimental

Reagents

Manipulations were generally carried out under dry, oxygen free nitrogen in Schlenk apparatus by Schlenk techniques [26]. Solvents were dried and purified by standard methods and freshly distilled before use. Chemical reagents were used as received. *trans*-$PtMeI(PPh_3)_2$ (**1**) and *trans*-$PdMeI(PPh_3)_2$ (**2**) were prepared by published methods [27]. Na(acac), Na(tfac) and Na(sacac) were prepared by reaction of NaOMe with corresponding β-diketonates in MeOH and recrystallized from MeOH/ether [28]. Tl(Ph-sacac) was prepared from the reaction of Tl(OAc) with Ph-sacacH in methanol.

Measurements

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

Infrared (IR) spectra were recorded in absorbance on a Digilab FTS 20E FT-IR spectrophotometer. Potassium bromide disks were used in the mid IR range (4000–500 cm^{-1}). Absorption bands (cm^{-1}) are described as strong (s), medium (m) or weak (w) in intensity.

Microanalyses were performed by the Central Science Laboratory, University of Tasmania.

Preparation of $PtMe(sacac)(PPh_3)$ (11)

To a solution of *trans*-$PtMeI(PPh_3)_2$ (0.18 g, 0.21 mmol) in THF (ca. 20 ml) was added $TlPF_6$ (0.073 g, 0.21 mmol) in THF (2 ml). The previously clear pale-yellow solution became cloudy. The mixture was stirred at room temperature for 3 h. A solution of Na(sacac) (0.04 g, 0.29 mmol) in methanol (2 ml) was added and a yellow precipitate immediately formed. The mixture was stirred at room tempera-

ture overnight. After evaporation of the solvent, the residue was extracted with CH_2Cl_2 (2 × 10 ml). TlI was filtered off through a Celite column, and the yellow filtrate was evaporated to dryness to leave an oily, yellow residue, which was treated with MeOH/petrolem ether (40–60 °C) to produce a yellow solid. This was crystallized from CH_2Cl_2/MeOH to give 0.1 g of yellow crystals (yield: 81%).

Anal. Found: C, 49.12; H, 4.46; S, 5.22. $C_{24}H_{25}OPSPt$ calcd.: C, 49.06; H, 4.29; S, 5.46%. IR (KBr, cm^{-1}): 1560s, 1480s (ν(C=O) and ν(C=C)). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 21.0 (J(PtP) = 3713 Hz). High resolution MS: Found: 586.104 calcd.: 586.099.

Preparation of PtMe(acac)(PPh$_3$) (4)

This complex was prepared by a similar method to that described for PtMe(sacac)(PPh$_3$) (**11**). PtMe(acac)(PPh$_3$) (**4**) was obtained as white crystals, yield: 75%.

Anal. Found: C, 50.64; H, 4.50. $C_{24}H_{25}O_2PPt$ calcd.: C, 50.43; H, 4.41%. IR (KBr, cm^{-1}): 1600s, 1570s (ν(C=O) and ν(C=C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 9.8 (J(PtP) = 4909 Hz). High resolution MS: found: 570.124, calcd.: 570.122.

Preparation of PtMe(tfac)(PPh$_3$) (5)

The complex was prepared by the method described for **11**. PtMe(tfac)(PPh$_3$) (**5**) was obtained as cream crystals from CH_2Cl_2/MeOH, yield: 76%.

Anal. Found: C, 47.3; H, 3.78. $C_{24}H_{22}F_3O_2PPt$ calcd.: C, 46.1; H, 3.55%. IR (KBr, cm^{-1}): 1620vs, 1580m, 1520s (ν(C=O) and ν(C=C)), 1260s, 1180s, 1120s, 1080s, 1000s (ν(C–F)). $^{31}P\{^1H\}$ NMR (C_6D_6): 2 isomers: δ 8.75 (^1J(PtP) = 4949 Hz); 7.42 (^1J(PtP) = 5011 Hz). High resolution MS: found for M: 624.089. calcd.: 624.094.

Preparation of PtMe(Ph-acac)(PPh$_3$) (6)

Prepared as previously described for **11**. **6** was obtained as a white crystals (yield: 84%).

Anal. Found: C, 55.61; H, 4.75. $C_{29}H_{27}O_2PPt$ calcd.: C, 54.97; H, 4.30%. IR (KBr cm^{-1}): 1580s, 1550vs, 1520vs, 1480s (ν(C=O) and ν(C=C)). High resolution MS: Found: 632.135, calcd: 632.137.

Preparation of PtMe(Ph-sacac)(PPh$_3$) (10)

The pale-yellow solution of *trans*-PtMeI(PPh$_3$)$_2$ (0.18 g, 0.21 mmol) in THF (ca. 20 ml) was added in portions to the THF solution (ca. 30 ml) of Tl(Ph-SacAc) (0.081 g, 0.21 mmol). The mixture was stirred at room temperature overnight and then filtered through a Celite column to remove TlI. The filtrate was evaporated to dryness to leave a red-orange oil, addition to which of ca. 1:1 MeOH/petroleum ether (40–60 °C) produced a red-orange solid, which was filtered off, and recrystallized from CH_2Cl_2/MeOH at −5 °C to give red-orange crystals (0.12 g, 86%).

Anal. Found: C, 52.5; H, 4.3. $C_{29}H_{27}OPSPt$ calcd.: C, 53.6; H, 4.2%. IR (KBr, cm^{-1}): 1540s, br (ν(C=O)). $^{31}P\{^1H\}$ NMR (C_6D_6): two isomers δ 21.2 (J(PtP) = 3723 Hz); 13.5 (J(PtP) = 4740 Hz). High resolution MS: found: 648.116, calcd.: 648.115.

Preparation of PdMe(acac)(PPh_3) (7)

The complex was prepared by the method described for **4**. Off-white crystals were obtained in a yield of 78%.

Anal. Found: C, 59.15; H, 5.59. $C_{24}H_{25}O_2PPd$ calcd.: C, 59.74; H, 5.22%. IR (KBr, cm^{-1}): 1580m, 1540s (ν(C=O) and ν(C=C)); $^{31}P\{^1H\}$ NMR (C_6D_6): 36.6.

Preparation of PdMe(sacac)(PPh_3) (13)

The complex was prepared by the method described for the complex **7**. PdMe(sacac)(PPh_3) (**13**) was obtained as yellow crystals by recrystallization from CH_2Cl_2/MeOH, yield: 73%.

Anal. Found: C, 57.87; H, 5.22; S, 5.97. $C_{24}H_{25}OPSPd$ calcd.: C, 57.82; H, 5.06; S, 6.44%. IR (KBr, cm^{-1}): 1580s, 1480s (ν(C=O) and ν(C=C)).

Preparation of PdMe(tfac)(PPh_3) (8)

Prepared by the method described for **7**. PdMe(tfac)(PPh_3) (**8**) was obtained as white crystals by recrystallization from CH_2Cl_2/MeOH, yield: 81%.

Anal. Found: C, 53.40; H, 4.28. $C_{24}H_{22}F_3O_2PPd$ calcd.: C, 53.74; H, 4.13%. IR (KBr, cm^{-1}): 1620vs, 1580m, 1520s (ν(C=O) and ν(C=C)), 1300vs, 1200s, 1140s, 1100s (ν(C–F)).

Preparation of PdMe(Ph-acac)(PPh_3) (9)

Prepared as described for **7**. PdMe(Ph-acac)(PPh_3) (**9**) was obtained as white crystals (yield: 83%).

Anal. Found: C, 62.91; H, 5.25. $C_{29}H_{27}O_2PPd$ calcd.: C, 63.92; H, 5.00%. IR (KBr, cm^{-1}): 1600vs, 1560vs, 1520vs, 1500s (ν(C=O) and ν(C=C)).

Preparation of PdMe(Ph-sacac)(PPh_3) (12)

Prepared in a similar manner to that described for the platinum analogue **10**. PdMe(Ph-sacac)(PPh_3) (**12**) was obtained as orange-red crystals after recrystallization from CH_2Cl_2/MeOH, yield: 83%.

Anal. Found: C, 58.94; H, 5.25; S, 4.46. $C_{29}H_{27}OPPdS$ calcd.: C, 62.12, H, 4.85; S, 5.72%. IR (KBr, cm^{-1}): 1580s, 1540s (ν(C=O) and ν(C=C)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.0.

Acknowledgements

We thank the Australian Research Council for financial support and for providing a Post-doctoral Research Associateship (to H.J.) We also thank Johnson Matthey Ltd. for their generous loan of palladium chloride and potassium tetrachloro-platinate.

References

1 P.W. Jolly in G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon, Oxford, 1982, p. 615.
2 D. Walther, Coord. Chem. Rev., 79 (1987) 135.
3 K.J. Cavell and E. Peacock, unpublished results.
4 (a) K.J. Cavell and A.F. Masters, J. Chem. Res., (1983) 72; (b) US Patent 4 533 651 to CSIRO; (c) K.J. Cavell and A.F. Masters, Aust. J. Chem., 39 (1986) 1129.

5 B. Bogdanovic, Adv. Organomet. Chem., 17 (1979) 105.
6 W. Keim, B. Hoffmann, R. Lodewick, M. Peuckert and G. Schmitt, J. Mol. Catal., 6 (1979) 79.
7 (a) R. Abeywickrema, M.A. Bennett, K.J. Cavell, A.F. Masters, M. Kony and A.G. Webb, in preparation; (b) K.J. Cavell, A.F. Masters and A.G. Webb, in preparation.
8 A.M.A. Bennett, G. Foulds, D.A. Thornton, K.J. Cavell and E.J. Peacock, in preparation.
9 N. Ishio, Y. Nakamura and S. Okeya, Bull. Chem. Soc. Jpn., 57 (1984) 1012.
10 D.A. Thornton, Coord. Chem. Rev., 104 (1990) 173.
11 S. Baba, T. Ogura and S. Kawaguchi, Bull. Chem. Soc. Jpn., 47 (1974) 665.
12 K. Yamada, S. Baba, Y. Nakamura and S. Kawaguchi, Bull. Chem. Soc. Jpn., 56 (1983) 1393.
13 P.E. Pregosin and R.W. Kunz, ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes, Springer-Verlag, Berlin, 1979.
14 C. Eaborn, K.J. Odell and A. Pidcock, J. Chem. Soc., Dalton Trans., (1978) 357.
15 T. Ito, T. Kiriyama and A. Yamamoto, Bull. Chem. Soc. Jpn., 49 (1976) 3250.
16 H. Jin, PhD Thesis, Australian National University, 1990, p. 163.
17 H.E. Bryndza, S.A. Kretchmar and T.H. Tulip, J. Chem. Soc., Chem. Commun., 977 (1985).
18 T.G. Appleton and M.A. Bennett, Inorg. Chem., 17 (1978) 739.
19 T. Ito, T. Kiriyama, Y. Nakamura and A. Yamamoto, Bull. Chem. Soc. Jpn., 49 (1976) 3257.
20 A. Yamamoto, T. Yamamoto, T. Saruyama and Y. Nakamura, J. Am. Chem. Soc., 95 (1973) 4073.
21 J.M. Huggins and R.G. Bergman, J. Am. Chem. Soc., 103 (1981) 3002.
22 D.L. Reger, J.C. Baxter and D.G. Garza, Organometallics, 9 (1990) 16.
23 J. Browning, K.A. Beveridge, G.W. Bushnell and K.R. Dixon, Inorg. Chem., 25 (1986) 1987.
24 R.C. Mehrotra, R. Bohra and D.P. Gaur, Metal β-Diketonates and Allied Derivatives, Academic Press, London, 1978, p. 245 and references cited therein.
25 M.A. Bennett, K.J. Cavell and K.Y. Chan, Inorg. Chim. Acta, 163 (1989) 153.
26 D.F. Shriver and M.A. Drezdzon, The Manipulation of Air-Sensitive Compounds, 2nd ed., John Wiley & Sons, New York, 1986.
27 P.E. Garrou and R.F. Heck, J. Am. Chem. Soc., 98 (1976) 4115.
28 O. Siimann and J. Fresco, J. Chem. Phys., 54 (1971) 734.