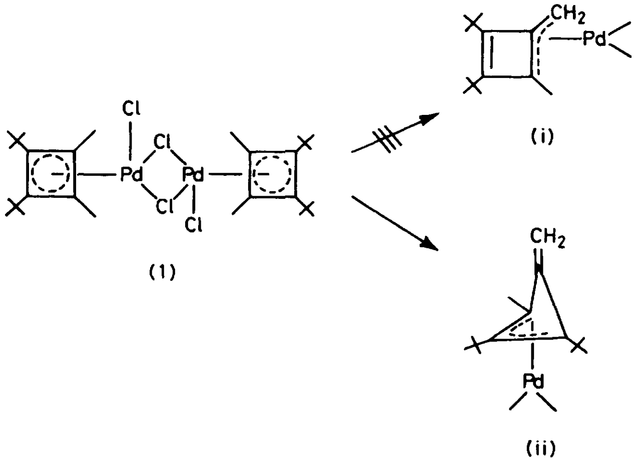
Synthesis and Characterisation by Spectroscopy and *X*-Ray Structure Determination of Palladium Complexes containing the 1—3-η-1,2-Di-t-butyl-3-methyl-4-methylenecyclobutenyl ligand

By **Philip J. Ridgwell, Pamela M. Bailey, Stuart N. Wetherell, Elizabeth A. Kelley, and Peter M. Maitlis,*** Department of Chemistry, The University, Sheffield S3 7HF

The (1,2-di-t-butyl-3,4-dimethylcyclobutadiene)palladium complex $[Pd_2\{C_4(Me)_2(Bu^t)_2\}_2Cl_4]$ reacts with base with loss of HCl to give $[Pd_2\{C_4{:}CH_2(Me)(Bu^t)_2\}_2Cl_2]$ (2). An *X*-ray crystal structure determination on the acetylacetonato-derivative $[Pd\{C_4{:}CH_2(Me)(Bu^t)_2\}(acac)]$ (3) shows the acetylacetonatopalladium 1—3-η-bonded to a cyclobutenyl ligand bearing an unco-ordinated methylene substituent at C^4, t-butyl groups at C^1 and C^2, and a methyl at C^3. N.m.r. (^1H and ^{13}C) spectroscopy showed that the ligand in (2) had the same structure. This was also true of the following derivatives that were synthesised: $[Pd_2(A)_2X_2]$ (X = Br, I, or SCN), $[Pd(A)(L)Cl]$ (L = Bu^tNC, p-ClC_6H_4NC, p-$MeC_6H_4NH_2$, PMe_2Ph, $PMePh_2$, PPh_3, or py), $[Pd(A)L_2]^+$ [L = $SC(NH_2)_2$, L_2 = $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, 2,2′-bipyridyl, 1,10-phenanthroline, or cyclo-octa-1,5-diene] and $[Pd(A)(S_2CNR_2)]$ (R = Et or Pr^i) [A = $\{C_4{:}CH_2(Me)(Bu^t)_2\}$].

SOME time ago we reported the preparation and structural characterisation of some (1,2-di-t-butyl-3,4-dimethylcyclobutadiene)palladium complexes including compound (1) (below).[1,2] We subsequently found that this (and related complexes) reacted with a variety of reagents including pyridine, t-butyl isonitrile, or Tl(acac) † to give η^3-allylic complexes in which a proton had been lost from one of the ring methyls.[3] Reaction with HCl regenerated the cyclobutadiene complex (1) and we concluded that no major structural reorganisation involving the C_4 ligand had taken place. On the basis of their ^1H n.m.r. spectra we originally supposed that the η^3-bonding was exocyclic and that an η^3-dehydrocyclobutadiene structure (i) had been formed. This idea was strengthened by the compounds which Shaw and coworkers[4] prepared by deprotonation of (hexamethylbicyclo[2.2.0]hexadiene)-palladium(II) or -platinum(II) complexes and for which just such an exocyclic η^3-allylic bonding had been established. An improved route to these complexes has now enabled us to obtain crystals, one of which was suitable for *X*-ray analysis. This showed that the ligand had a η^3-methylenecyclobutenyl structure (ii).



(1)

(i)

(ii)

RESULTS AND DISCUSSION

Reaction of (1) with sodium carbonate in dichloromethane gave complex (2), of empirical formula $(C_{14}H_{23}ClPd)_n$; an osmometric molecular weight measurement showed $n = 2$. In other words, one molecule of (1) had lost two moles of HCl to give (2). From the far-i.r. spectrum [ν(Pd–Cl) 232m and 261s cm^{-1}] we deduced that (2) is a chlorine-bridged dimer of the conventional type $[(A)PdCl_2Pd(A)]$ where A is an η^3-allylic ligand. The ^1H n.m.r. spectrum in C_6D_6 showed the presence (Table 1) of two inequivalent t-butyl groups, one methyl, and two singlets (δ 3.72, 3.63) each of relative intensity corresponding to 1 H, which were due to a methylene group. The ^{13}C-$\{^1H\}$ n.m.r. spectrum showed the easily assigned singlet resonances at δ 12.3 (CH_3), 28.6, 30.7 $[C(CH_3)_3]$, 33.1, 33.7 $[C(CH_3)_3]$, as well as five more at δ 78.7, 94.9, 106.3, 133.5, and 138.4. These could be assigned to the CH_2 and the four ring carbons of either structure (i) or (ii) based upon known analogies.[5] On cooling (to −60 °C) all these resonances split (Table 2); in some cases four lines were seen but accidental coincidence frequently reduced the number. This effect was due to the presence of various geometric isomers. Similar observations have been made on other dimeric allylic palladium chloride complexes where the allylic ligands were both bulky and chiral.[6] Such isomerism becomes obvious when rotation (or exchange) about the Pd_2Cl_2 group is sufficiently slowed down on the n.m.r. time-scale by cooling.

This isomerism was absent in the mononuclear acetylacetonato-complex (3) derived (in 82% yield) from (2) by reaction with Tl(acac). Except for the acac resonances, however, the ^1H and ^{13}C n.m.r. spectra of the two complexes were virtually identical. Attempts to determine the structure of a crystal of the dinuclear complex (2) were frustrated by pseudo-symmetry problems in the Patterson vector map. However, crystals of complex (3) proved more amenable and a complete *X*-ray structure analysis was carried out.

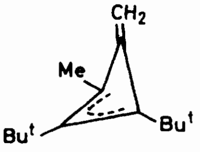
This showed (Figure and Table 3) that the Pd(acac) moiety is η^3-bonded to the three ring carbons, C(1), C(2),

---

† acac = Acetylacetonate.

TABLE 1

^{1}H n.m.r. spectroscopic data (δ) [a]



A

	Complex	CH_2	Me	Bu^t	Other
(2)	$[Pd_2(A)_2Cl_2]$	3.76, 3.71	1.44	1.44, 1.31	
(2)	$[Pd_2(A)_2Cl_2]$ [b]	3.72, 3.63	1.31	1.35, 1.25	
(3)	[Pd(A)(acac)]	3.62, 3.56	1.29	1.36, 1.29	5.24 (1 H, acac-*H*) 1.81 (6 H, acac-*Me*)
(6)	$[Pd_2(A)_2Br_2]$	3.83, 3.75	1.57	1.43, 1.36	
(7)	$[Pd_2(A)_2I_2]$	3.91, 3.83	1.80	1.44, 1.41	
(8)	$[Pd_2(A)_2(SCN)_2]$	3.83, 3.71	1.53	1.38, 1.35	
(9)	$[Pd(A)(Bu^tNC)Cl]$ [c]	3.98, 3.85	1.66	1.33, 1.29	1.56 (9 H, Bu^tNC) 1.43 (Bu^tNC unco-ordinated)
(10)	$[Pd(A)(p\text{-}ClC_6H_4NC)Cl]$	3.83, 3.78	1.58	1.40, 1.29	6.83 (dd, 4 H, ClC_6H_4NC)
(11)	$[Pd(A)(p\text{-}MeC_6H_4NH_2)Cl]$	3.77, 3.71	1.42	1.42, 1.33	6.74 (dd, 4 H, $MeC_6H_4NH_2$) 2.19 (s, 3 H, $MeC_6H_4NH_2$) 2.83 (s, 2 H, $MeC_6H_4NH_2$)
(12)	$[Pd(A)(PMe_2Ph)Cl]$	4.02, 3.73	1.78 [d, *J*(PH) = 4]	1.32, 1.23	7.39—7.80 (m, 5 H, *Ph*-P)
(13)	$[Pd(A)(PMePh_2)Cl]$ [d]	4.05, 3.97	2.05 [d, *J*(PH) = 4]	1.27, 1.19	7.38 (br, 10 H, *Ph*–P) 1.65 [d, *J*(PH) = 4, 6 H, *Me*–P] 1.38 [d, *J*(PH) = 4, 3 H, *Me*–P]
(14)	$[Pd(A)(PPh_3)Cl]$	4.10, 3.83	2.06 [d, *J*(PH) = 4]	1.55, 1.23 (br)	7.39—7.85 (m, 15 H, Ph)
(15)	[Pd(A)(py)Cl]	3.79, 3.70	1.73	1.41, 1.34	7.33—7.80 (m, 5 H, C_5H_5N)
(16)	$[Pd(A)\{SC(NH_2)_2\}_2]Cl$	4.64, 4.52	1.32	1.20	7.37 (br, s, 4 H, NH_2)
(17)	[Pd(A)(dppm)]Cl	4.81, 4.75	1.32	1.52, 1.11	7.46 (br, 20 H, dppm) 4.10 (br, 4 H, dppm)
(18)	$[Pd(A)(bipy)][PF_6]$	4.29, 4.22	1.99	1.64, 1.43	7.86—9.22 (m, 8 H, bipy)
(19)	$[Pd(A)(phen)][PF_6]$	4.20, 4.13	2.03	1.69, 1.45	8.05—9.48 (m, 8 H, phen)
(20)	$[Pd(A)(dppe)][PF_6]$ [e]	4.87, 4.83	1.30 [d, *J*(PH) = 5]	1.01, 0.93	7.3—7.9 (m, 20 H, dppe) 1.95 [t, *J*(PH) = 4, 4 H, dppe]
(21)	$[Pd(A)(cod)][PF_6]$	4.82, 4.73	2.01	1.43, 1.40	6.37, 6.00, 5.86 (4 H, cod) 2.56, 2.61 (8 H, cod)
(27)	$[Pd(A)(S_2CNEt_2)]\cdot H_2O$ [c]	3.80, 3.70	1.70	1.39, 1.28	3.75 [q, *J* = 7, 4 H, CH_2CH_3] 1.31 [t, *J* = 7, 6 H, CH_2CH_3] 3.03 (s, H_2O)
(28)	$[Pd(A)(S_2CNPr^i_2)]\cdot H_2O$	3.74, 3.65	1.78	1.50, 1.33	1.40 [br, 12 H, $CH(CH_3)_2$]

[a] All peaks were sharp singlets and the spectra were recorded in $(CD_3)_2CO$ unless otherwise stated; $SiMe_4$ was used as internal standard. [b] Recorded in C_6D_6. [c] Recorded at −60 °C. [d] Recorded in $CDCl_3$. [e] Recorded in $CDCl_3$ at −60 °C.

and C(3), of a C_4 ring [Pd–C(mean) 2.108 Å]. The fourth carbon, C(4), is very significantly (45σ) further from the metal [2.425(7) Å] and is really out of direct bonding range [as in (ii)]. This carbon is also attached by a rather short bond [1.359(12) Å] to C(5) which is therefore the *exo*-methylene group seen in the ^{1}H n.m.r. spectrum. Support for this formulation comes from the dihedral angle of 20.4° between the planes C(1)–C(2)–C(3) and C(1)–C(4)–C(3), with C(4) bent away from the metal. Atom C(5) is only 0.06 Å out of the plane C(1)–C(4)–C(3) and is therefore virtually coplanar with it. The out-of-plane distance of the metal to C(1)–C(2)–C(3) is 1.84 Å.

The structure of the C_4 ligand of complex (3) is very close to that for the C_4 ligand in the (η^3-1-keto-2,3,4-triphenylcyclobutenyl)cobalt complex (4) [7] in all significant respects. However, in complex (4) the dihedral angle in the C_4 ring is only 11° even though the distance of the cobalt to the C(Ph) carbons [mean 2.07 Å] is again significantly less than that to the ring keto-carbon (2.40 Å).

It is evident from our structure determination of complex (3) that the η^3-cyclobutenyl type of bonding (ii) is appreciably favoured over the exocyclic ' dehydrocyclobutadiene ' form (i). Presumably complexation to

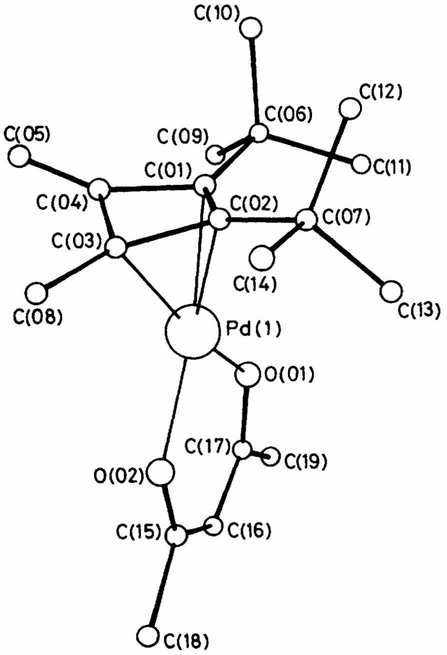
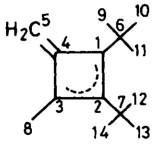


FIGURE Structure of $[Pd\{\eta^3\text{-}C_4{:}CH_2(Me)(Bu^t)_2\}(acac)]$ (3), showing the atom numbering the metal relieves the strain in the C_4 ring appreciably and this is much more significant than any gain that arises from stabilising the exocyclic allylic grouping.

TABLE 2

$^{13}C-\{^1H\}$ n.m.r. spectroscopic data (δ) [a]

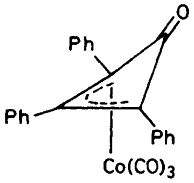


A

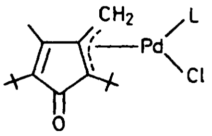
	Complex	$C^{2,5}$	$C^{1,3}$	C^4	C^8	$C^{6,7}$	C^{9-14}	Other
(3)	[Pd(A)(acac)]	140.8	96.3	77.2	10.9	34.0, 33.5	30.9, 28.7	188.6 (acac-*C*O)
		135.0	86.3					99.7 (acac-*C*H)
								10.9 (acac-*C*H_3)
(2)	[$Pd_2(A)_2Cl_2$] [b]	138.4	106.3	78.7	12.3	33.7, 33.1	30.7, 28.6	
		133.5	94.9					
(2)	[$Pd_2(A)_2Cl_2$] [c]	138.2	106.6	78.9	12.7	33.6, 32.9	30.5, 29.0	
		138.1	106.4	78.7	12.6	33.5, 32.8	30.4, 28.2	
		138.0	106.1	78.3	12.4	33.4, 32.0		
		133.9	105.9		12.2			
		133.8	95.2					
		133.7	94.9					
			94.6					
			94.4					
(8)	[$Pd_2(A)_2(SCN)_2$]	136.9	104.4	80.0	12.0	33.5, 33.1	30.5, 29.7	
		130.7	93.8					
(16)	[Pd(A){$SC(NH_2)_2$}$_2$]Cl	137.7	110.1	80.0	11.6	35.0, 32.1	30.6, 29.1	203.8 (S*C*NH_2)
		136.6						
(18)	[Pd(A)(bipy)][PF_6]	138.9	100.3	77.8	11.9	33.9, 32.4	30.1, 28.7	154.2, 153.7, 149.7,
		134.2	91.6					126.8, 120.3, 138.0 (bipy)
(21)	[Pd(A)(cod)][PF_6] [b]	138.2	102.1	78.7	12.0	33.7, 33.0	29.9, 28.6	130.4, 27.7, 26.9 (cod)
		130.9	91.4					

[a] In $(CD_3)_2CO$ unless otherwise stated. [b] Recorded in $CDCl_3$. [c] Recorded in $CDCl_3$ at −60 °C.

It is interesting to contrast this structure with the one adopted by the deprotonated form of the (2,5-di-t-butyl-3,4-dimethylcyclopentadienone)palladium complex. In that case there seems little alternative to the structure (5), with an exocyclic η^3-allylic group, that was originally proposed, and which showed the complexed allylic CH_2 as a triplet at δ 59.9 in the ^{13}C n.m.r. spectrum.[8] A dependence of the mode of binding on ring size has been noted by Hüttel *et al.*[9] who found that reaction of 1-methylcycloalkenes with palladium chloride gave the endocyclic allylic complex for the six-membered ring and exocyclic allylic complexes for the seven-, eight-, ten-, and twelve-membered rings.



(4)



(5)

A range of other derivatives of [Pd{C_4:CH_2(Me)-$(Bu^t)_2$}], [Pd(A)], have been prepared (Scheme); from their ^1H and ^{13}C spectra (Tables 1 and 2) it is clear that the same organic ligand is present in all of them. To ensure that no isomerisation had occurred on dissolving (3) at ambient temperature, a sample was dissolved at −78 °C in dichloromethane. The n.m.r. spectrum was identical to that obtained from a sample made up in the normal way. We may conclude from this experiment and from the absence of any change in the spectrum with

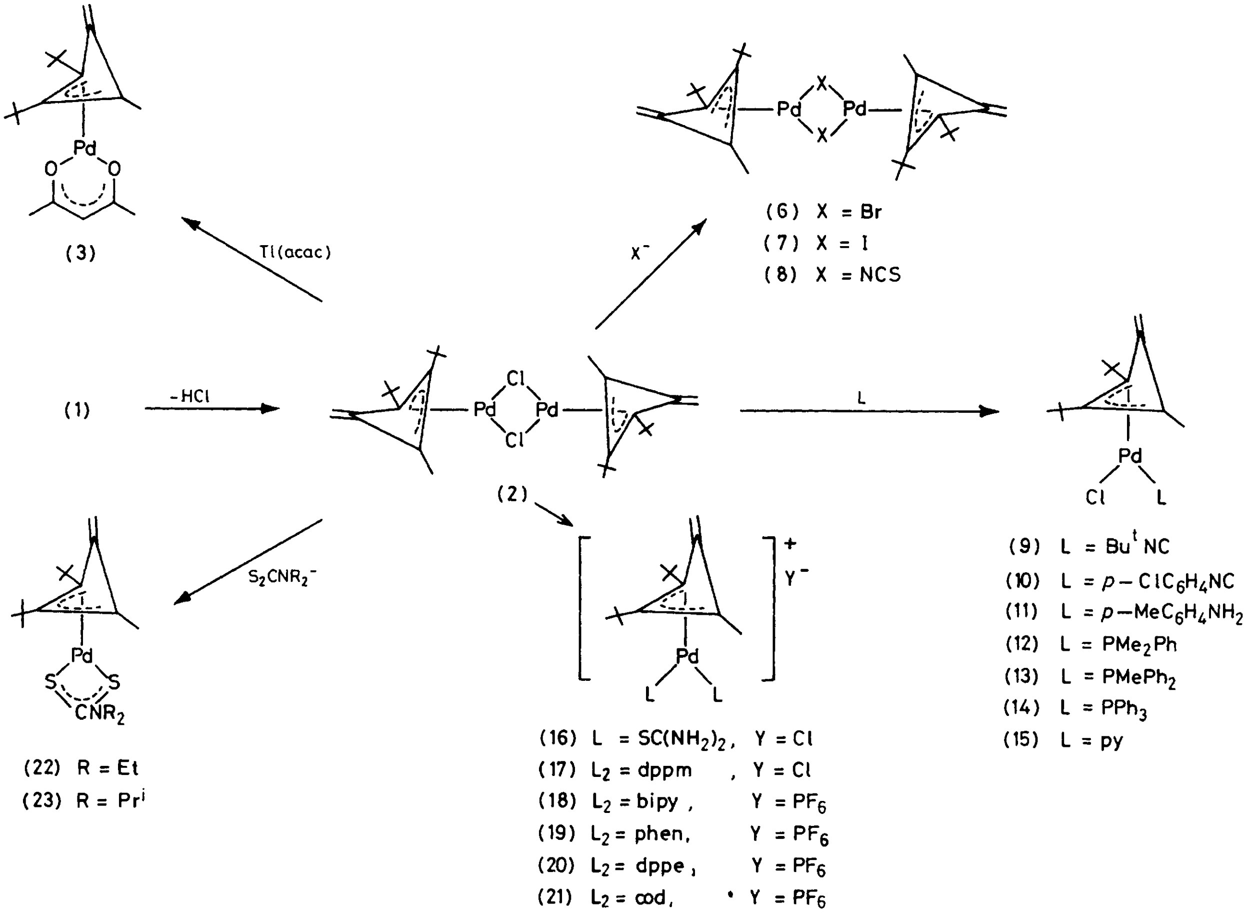
TABLE 3

Selected bond lengths (Å) and angles (°) for [Pd{η^3-C_4:CH_2-(Me)$(Bu^t)_2$}(acac)] (3), with estimated standard deviations in parentheses

(*a*) Distances			
Pd–C(1)	2.101(7)	C(1)–C(6)	1.511(10)
Pd–C(2)	2.120(7)	C(2)–C(7)	1.529(10)
Pd–C(3)	2.103(7)	C(3)–C(8)	1.522(12)
Pd–C(4)	2.425(7)	C(4)–C(5)	1.359(12)
Pd–O(1)	2.078(5)	C(1)–C(3)	2.043(10)
Pd–O(2)	2.097(5)	C(2)–C(4)	2.079(10)
C(1)–C(2)	1.470(10)		
C(2)–C(3)	1.432(10)		
C(3)–C(4)	1.481(10)		
C(4)–C(1)	1.495(10)		
(*b*) Angles			
O(1)–Pd–C(3)	162.5(2)	C(6)–C(1)–C(2)	137.2(6)
O(1)–Pd–C(1)	108.2(1)	C(6)–C(1)–C(4)	129.0(6)
O(2)–Pd–C(3)	104.2(2)	C(7)–C(2)–C(1)	138.2(6)
O(2)–Pd–C(1)	162.0(1)	C(7)–C(2)–C(3)	132.1(6)
		C(8)–C(3)–C(2)	137.4(7)
C(1)–Pd–C(3)	58.2(3)		
		C(8)–C(3)–C(4)	128.9(7)
C(2)–Pd–C(4)	53.9(2)		
		C(5)–C(4)–C(3)	133.3(7)
C(1)–C(2)–C(3)	89.5(5)	C(5)–C(4)–C(1)	133.9(7)
C(2)–C(3)–C(4)	91.0(6)		
C(3)–C(4)–C(1)	86.7(5)		
C(4)–C(1)–C(2)	89.0(5)		
C(2)–C(4)–C(5)	167.0(7)		
C(1)–C(3)–C(8)	175.6(6)		
C(3)–C(1)–C(6)	172.8(6)		

change in temperature that no significant amount of any *exo*-allylic isomer such as (i) is present and that the spectra of solutions of these complexes are the spectra of the ligand as in (ii).

The complexes (6)—(8), (22), and (23) were prepared by metathesis with NaBr, NaI, KCNS, or Na[S_2CNR_2] respectively. Reaction of the dinuclear complex (2) with monodentate ligands (L) gave the complexes (9)—(15).



SCHEME dppm = Bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, bipy = 2,2′-bipyridyl, phen = 1,10-phenanthroline, cod = cyclo-octa-1,5-diene

Reaction of (2) with excess thiourea or bis(diphenylphosphino)methane (dppm) gave the ionic chlorides (16) or (17) respectively. This was shown by the absence of any strong bands, ν(Pd–Cl), in the i.r. spectra below 400 cm^{-1} and by the conductivity of (16) in nitromethane (53 Ω^{-1} mol^{-1} cm^2) compared with that of a known 1 : 1 electrolyte, tetrabutylammonium chloride (48 Ω^{-1} mol^{-1} cm^2).

The other ionic complexes (18)—(21) were prepared by addition of silver hexafluorophosphate to an acetone solution of complex (2). This generated a labile solvent species, presumably [Pd{C_4:CH_2(Me)(Bu^t)$_2$}(Me$_2$CO)$_2$]$^+$-PF$_6^-$, the solvent molecules in which could be readily displaced by reaction with the appropriate bidentate ligand, L$_2$. It was noted that the CH$_2$ signals in the ^{1}H n.m.r. spectra were shifted to lower field in the ionic complexes. Exchange processes with ligands were detected for (17) and also for the isonitrile complex (10). These were frozen out at low temperature (−60 °C).

The monomeric phosphine complexes (12)—(14) showed the ring methyl as a doublet [J(P–H) = 4 Hz] in each case and indicated the absence of any fast exchange. The small size of this coupling to phosphorus is consistent [10] with the stereochemistry expected on steric grounds, with the phosphine *cis* to the methyl group, and *trans* to the bulky t-butyl.

Our attempts to add a further metal to the free exocyclic methylene were unsuccessful, but this may arise from a high kinetic barrier rather than from any inherent inability of this double bond to complex.

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen but none of the complexes was appreciably air-sensitive. Microanalyses (collected in Table 4) were determined by the Department of Chemistry Microanalytical Service, n.m.r. spectra (collected in Tables 1 and 2) were run on Perkin-Elmer R-12B (^{1}H, 60 MHz) or Jeol PFT-100 (^{13}C) spectrometers, and far-i.r. spectra (Table 4) were measured on a Perkin-Elmer 180 spectrometer. Typical preparations are given below, yields are quoted in Table 4.

$[Pd_2\{C_4{:}CH_2(Me)(Bu^t)_2\}_2Cl_2]$ (2).—Anhydrous sodium carbonate (0.96 g, 9 mmol) was added to a stirred solution of complex (1) (2.2 g, 3 mmol) in dichloromethane (30 cm³). After 15 h at 20 °C the solids were filtered off and the filtrate reduced to dryness. The residue was crystallised from acetone as yellow platelets. Yield, 1.46 g (73%).

TABLE 4

Yields and microanalytical and i.r. spectroscopic data for [Pd(A)XY] complexes $[A = \eta^3\text{-}\{C_4{:}CH_2(Me)(Bu^t)_2\}]$

	Complex	Yield (%)	Microanalytical data * (%) C	H	N	Other	I.r. (cm⁻¹)
(2)	$[Pd_2(A)_2Cl_2]$	73	50.5 (50.5)	6.8 (6.9)		Cl, 10.8 (10.7) *M*, 697 (666)	ν(PdCl) 232m, 261s
(3)	[Pd(A)(acac)]	82	56.9 (57.4)	7.5 (7.6)			
(6)	$[Pd_2(A)_2Br_2]$	89	44.5 (44.5)	6.1 (6.1)		Br, 22.0 (21.2) *M*, 736 (755)	ν(PdBr) 167m
(7)	$[Pd_2(A)_2I_2]$	91	40.0 (39.6)	5.4 (5.4)		I, 30.1 (29.9)	ν(PdI) 138m
(8)	$[Pd_2(A)_2(SCN)_2]$	86	50.4 (50.7)	6.4 (6.4)	3.9 (3.9)	S, 9.1 (9.0)	ν(SCN) 2 085vs
(9)	$[Pd(A)(Bu^tNC)Cl]$	78	54.9 (54.8)	7.7 (7.7)	3.7 (3.4)	Cl, 8.4 (8.5)	ν(PdCl) 312s ν(NC) 2 185vs
(10)	$[Pd(A)(p\text{-}ClC_6H_4NC)Cl]$	59	53.7 (53.6)	5.7 (5.7)	2.9 (3.0)	Cl, 15.2 (15.1)	ν(PdCl) 303s ν(NC) 2 205vs
(11)	$[Pd(A)(p\text{-}MeC_6H_4NH_2)Cl]$	78	56.8 (57.2)	7.3 (7.3)	3.2 (3.2)	Cl, 8.6 (8.1)	
(12)	$[Pd(A)(PMe_2Ph)Cl]$	64	56.1 (56.1)	7.2 (7.0)		Cl, 7.7 (7.5)	ν(PdCl) 317m
(13)	$[Pd(A)(PMePh_2)Cl]$	69	61.0 (60.8)	6.8 (6.7)		Cl, 6.7 (6.7)	ν(PdCl) 309m
(14)	$[Pd(A)(PPh_3)Cl]$	77	64.6 (64.6)	6.4 (6.4)		Cl, 6.0 (6.1)	ν(PdCl) 314s
(15)	[Pd(A)(py)Cl]	14	55.4 (55.4)	6.8 (6.8)	3.3 (3.4)	Cl, 8.7 (8.6)	
(16)	$[Pd(A)\{SC(NH_2)_2\}_2]Cl$	72	39.6 (39.6)	6.4 (6.4)	11.7 (11.5)	Cl, 7.3 (7.3) S, 13.5 (13.2)	
(17)	[Pd(A)(dppm)]Cl	95	65.4 (65.3)	6.3 (6.3)		Cl, 4.7 (4.9)	
(18)	$[Pd(A)(bipy)][PF_6]$	68	48.4 (48.1)	5.2 (5.2)	4.8 (4.6)		
(19)	$[Pd(A)(phen)][PF_6]$	67	50.3 (50.1)	5.1 (5.0)	4.6 (4.6)		
(20)	$[Pd(A)(dppe)][PF_6]$	58	57.1 (57.1)	5.6 (5.6)			
(21)	$[Pd(A)(cod)][PF_6]$	61	48.0 (48.0)	6.4 (6.4)			
(22)	$[Pd(A)(S_2CNEt_2)]\cdot H_2O$	63	48.8 (49.2)	7.1 (7.5)	3.0 (3.0)	S, 13.7 (13.8)	ν(OH) 1 620w, 3 390w
(23)	$[Pd(A)(S_2CNPr^i{}_2)]\cdot H_2O$	42	51.2 (51.3)	7.5 (7.9)	2.9 (2.8)	S, 12.9 (13.0)	ν(OH) 1 635w, 3 400w,br

* Calculated values in parentheses.

$[Pd\{C_4{:}CH_2(Me)(Bu^t)_2\}(acac)]$ (3).—Acetylacetonatothallium (0.18 g, 0.6 mmol) was added to a stirred solution of complex (2) (0.2 g, 0.3 mmol) in acetone (20 cm³) at 0 °C. An immediate reaction occurred with precipitation of thallium chloride. This was removed by filtration and the filtrate was reduced in volume to 5 cm³. The solution was allowed to stand at 5 °C and the product was obtained as clear yellow crystals. Yield, 0.19 g (82%). One of these crystals proved suitable for an *X*-ray structure determination.

$[Pd_2\{C_4{:}CH_2(Me)(Bu^t)_2\}_2Br_2]$ (6).—Excess sodium bromide (0.25 g, 2.5 mmol) was added to a stirred solution of complex (2) (0.2 g, 0.3 mmol) in acetone (15 cm³). After 0.5 h at 20 °C the solution was filtered and the filtrate was reduced to dryness. The product was crystallised from acetone. Yield, 0.2 g (89%).

$[Pd\{C_4{:}CH_2(Me)(Bu^t)_2\}(Bu^tNC)Cl]$ (9).—t-Butyl isonitrile (0.05 g, 0.6 mmol) was added dropwise to a stirred solution of complex (2) (0.2 g, 0.3 mmol) in acetone (20 cm³). After 0.5 h/20 °C the solution was reduced to dryness and the residue was washed with light petroleum (b.p. 40—60 °C; 3 × 10 cm³). Crystals were obtained from an acetone solution of the washed residue by slow evaporation at 5 °C. Yield, 0.19 g (78%).

$[Pd\{C_4{:}CH_2(Me)(Bu^t)_2\}(py)Cl]$ (15).—Pyridine (py) (0.35 g, 4.4 mmol) was added slowly to a stirred suspension of complex (1) (2 g, 2 mmol) in dichloromethane (30 cm³). After 1 h/20 °C the suspension cleared and the dichlorobis(pyridine)palladium formed during the reaction was filtered off. Anhydrous sodium carbonate (0.96 g, 9 mmol) was added to the filtrate and the suspension stirred for 15 h. The solids were filtered off and the filtrate reduced to dryness. After extraction with light petroleum (b.p. 40—60 °C; 5 × 25 cm³) the required product was left as a light brown solid. Yield, 0.17 g (14%).

$[Pd\{C_4{:}CH_2(Me)(Bu^t)_2\}\{SC(NH_2)_2\}_2]Cl$ (16).—Excess thiourea (0.1 g, 1.2 mmol) was added to a stirred solution of complex (2) (0.2 g, 0.3 mmol) in acetone (20 cm³). After 3 h/20 °C the solution was reduced to dryness and the product extracted with dichloromethane (3 × 10 cm³). The solution was reduced to dryness and crystals obtained from an acetone solution at 5 °C. Yield, 0.18 g (72%).

$[Pd\{C_4{:}CH_2(Me)(Bu^t)_2\}(dppm)]Cl$ (17).—Bis(diphenylphosphino)methane (0.24 g, 0.6 mmol) was added to a stirred solution of complex (2) (0.2 g, 0.3 mmol) in acetone (30 cm³). After 3 h/20 °C the solution was reduced to a volume of 5 cm³ and the product was precipitated by the addition of light petroleum (b.p. 40—60 °C; 20 cm³). The yellow powder was washed with light petroleum (b.p. 40—60 °C; 3 × 10 cm³) and dried. Yield, 0.41 g (95%).

$[Pd\{C_4{:}CH_2(Me)(Bu^t)_2\}(bipy)][PF_6]$ (18).—Silver hexafluorophosphate (0.16 g, 0.6 mmol) was added to a stirred solution of complex (2) (0.2 g, 0.3 mmol) in acetone (25 cm³). An immediate reaction occurred with precipitation of silver chloride which was removed by filtration through cellulose. 2,2′-Bipyridyl (bipy) (0.094 g, 0.6 mmol) was added to the filtrate and the mixture stirred for 0.25 h. The solution was reduced to a volume of 5 cm³ and left to crystallise at 5 °C. Yield, 0.24 g (68%).

$[Pd\{C_4{:}CH_2(Me)(Bu^t)_2\}(S_2CNEt_2)]\cdot H_2O$ (22).—Hydrated sodium diethyldithiocarbamate (0.15 g, 0.6 mmol) was added to a stirred solution of complex (2) (0.2 g, 0.3 mmol) in acetone (25 cm³). After 0.5 h the solution was reduced to dryness and the product extracted with dichloromethane

($3 \times 10\ cm^3$). Addition of light petroleum (b.p. 40—60 °C; 30 cm^3) precipitated the product. Yield, 0.15 g (63%).

X-Ray Crystal Structure Determination of [Pd{C_4:CH_2(Me)-(Bu^t)$_2$}(acac)] (3).—*Crystal data.* $C_{19}H_{30}O_2Pd$, $M = 396.9$, Monoclinic, $a = 12.311(6)$, $b = 12.368(4)$, $c = 12.672(7)$ Å, $\beta = 84.30(4)°$, $U = 1\,920$ Å^3, $Z = 4$, $D_c = 1.37$ g cm^{-3}, $F(000) = 824$. Systematic absences are consistent with space group $P2_1/n$ (non-standard setting of C_{2h}^5, no. 14), Mo-K_α radiation (graphite monochromator) $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 9.6 cm^{-1}.

TABLE 5

Atomic co-ordinates ($\times 10^5$ for Pd, $\times 10^4$ for other atoms), with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Pd(1)	2 552(4)	14 191(4)	19 738(4)
O(01)	1 501(4)	1 232(4)	756(4)
O(02)	−43(4)	−249(4)	1 950(4)
C(01)	154(5)	3 065(5)	2 383(5)
C(02)	−76(5)	2 400(5)	3 340(5)
C(03)	−1 072(5)	2 048(6)	2 956(5)
C(04)	−1 007(6)	2 928(6)	2 159(5)
C(05)	−1 751(7)	3 387(9)	1 573(7)
C(06)	962(7)	3 932(6)	1 992(6)
C(07)	417(7)	2 197(7)	4 383(5)
C(08)	−2 047(7)	1 349(8)	3 349(7)
C(09)	970(8)	4 008(8)	768(7)
C(10)	587(10)	5 026(7)	2 507(9)
C(11)	2 146(7)	3 639(9)	2 244(7)
C(12)	592(9)	3 284(8)	4 922(7)
C(13)	1 505(8)	1 587(9)	4 179(7)
C(14)	−396(9)	1 511(9)	5 115(7)
C(15)	449(6)	−898(6)	1 293(6)
C(16)	1 243(6)	−650(6)	471(5)
C(17)	1 695(6)	360(6)	246(5)
C(18)	95(8)	−2 087(7)	1 455(8)
C(19)	2 534(7)	464(7)	−729(6)

Single-crystal *X*-ray data in the range $3.5 < 2\theta < 50°$ were collected on a Nicolet Instrument Syntex R3 four-circle diffractometer. For each reflection omega was scanned at a rate (dependent on pre-scan intensity) in the range 2.0—30.0° min^{-1}. 2 256 Independent reflections with $I > 3\sigma(I)$ and background $\Delta < 4\sigma(B)$ were corrected for Lorentz and polarisation effects but not for absorption or extinction. The structure was solved using Patterson and Fourier methods and refined using block diagonal-matrix least-squares refinement to $R = 0.042$. Calculations were computed on the Nicolet-Syntex XTL package and the University of Sheffield ICL 1906S computer using programs from the Sheffield *X*-ray system.

The overall geometry of the molecule is shown in the Figure. Atomic co-ordinates are in Table 5, bond distances and angles in Table 3. Tables of structure factors and the isotropic and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 23260 (26 pp.).*

We thank the S.E.R.C. for supporting this work, the University of Sheffield for the award of a Junior Research Fellowship (to P. M. B.), Dr. B. E. Mann for helpful discussion, and Mr. G. A. Wright for the preparation of starting materials.

[1/1796 *Received*, 18*th November*, 1981]

REFERENCES

[1] E. A. Kelley, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1977, 289.

[2] E. A. Kelley and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 167.

[3] E. A. Kelley, Ph.D. Thesis, University of Sheffield, 1977.

[4] J. F. Malone, W. S. Macdonald, B. L. Shaw, and G. Shaw, *Chem. Commun.*, 1968, 869; B. L. Shaw and G. Shaw, *J. Chem. Soc. A*, 1969, 602.

[5] Y. Senda, H. Suda, J. Ishiyama, S. Imaizumi, A. Kasahara, T. Izumi, and T. Kato, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1608; S. H. Taylor and P. M. Maitlis, *J. Am. Chem. Soc.*, 1978, **100**, 4700; B. E. Mann and B. F. Taylor '^{13}C NMR Data for Organometallic Compounds,' Academic Press, London, 1981.

[6] See, for example, D. J. Mabbott and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1977, 254.

[7] J. Potenza, R. Johnson, D. Mastropaolo, and A. Efraty, *J. Organomet. Chem.*, 1974, **74**, C13.

[8] E. A. Kelley, G. A. Wright, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 178.

[9] R. Hüttel, H. Dietl, and H. Christ, *Chem. Ber.*, 1964, **97**, 2037; R. Hüttel and H. Dietl, *Chem. Ber.*, 1965, **98**, 1753.

[10] J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 1967, 1839; see also K. Vrieze, A. P. Praat, and P. Cossee, *J. Organomet. Chem.*, 1968, **12**, 533.

---

* For details see Notices to Authors No, 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.