Journal of Organometallic Chemistry, 327 (1987) 101–114
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CYCLOMETALLATED COMPOUNDS

II *. PROTON AND CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRAL ASSIGNMENTS OF CYCLOPALLADATED COMPOUNDS

PETER J. STEEL* and GRAHAM B. CAYGILL
Chemistry Department, University of Canterbury, Christchurch (New Zealand)
(Received December 11th, 1986)

Summary

The ^{1}H and ^{13}C NMR spectra of nineteen cyclopalladated acetylacetonate complexes are reported. Definitive spectral assignments are made on the basis of selective proton decoupling experiments, difference NOE spectra and both homo- and hetero-nuclear two-dimensional correlation spectroscopy. The Pd(acac) substituent is shown to induce characteristic chemical shift changes in both proton and carbon spectra. These effects, however, vary from those of differently substituted palladium and other metal substituents.

Introduction

Since the initial discovery [1] of the facile cyclopalladation of azobenzene numerous related organopalladium compounds incorporating an intramolecular nitrogen donor have been reported [2–6]. Such compounds have proved to be versatile intermediates in organic synthesis [7]. In line with the increasing use of ^{13}C NMR for the study of organometallic compounds [8] there have been a number of ^{13}C NMR spectra of cyclopalladated compounds reported [9–19]. However, full assignments of such spectra have been made in only a few cases [15–19]. Furthermore, a survey of reported spectral data suggests unusual variations in the effect of cyclopalladation on ^{13}C NMR chemical shifts, and reveals a number of inconsistencies in some reported assignments.

Although ^{1}H NMR has frequently been used to demonstrate the occurrence of cyclopalladation, the spectra have seldom been fully assigned due to extensive overlap of signals in spectra recorded at low magnetic field strengths. However, such assignments become relatively straightforward at higher magnetic field strengths by

* For part I see ref. 19.

0022-328X/87/$03.50

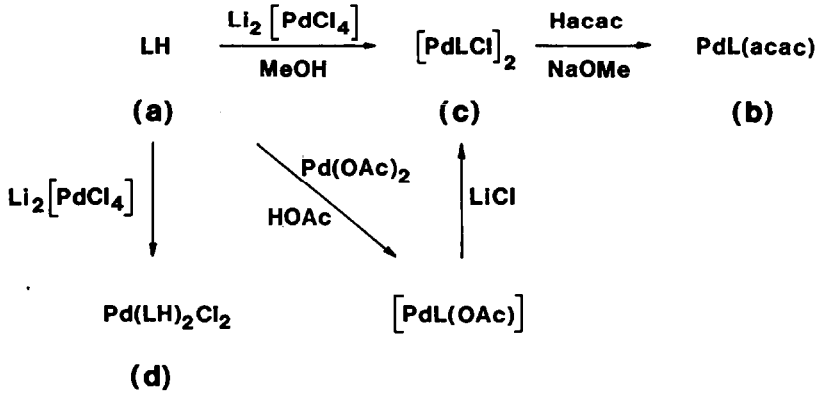
means of homonuclear correlated two-dimensional (2D) NMR spectroscopy [20,21]. The potential of such techniques is dramatically exemplified in recent reports [22–24] of full assignments for ^{1}H NMR spectra of complex (> 20 aromatic protons) cyclometallated ruthenium complexes. Furthermore, given a fully assigned ^{1}H NMR spectrum it is possible to definitively assign a ^{13}C NMR spectrum by means of heteronuclear correlated 2D NMR [20,21].

Although ^{13}C NMR chemical shift data provide important structural information, it has been noted in a recent review [4] that there is "a dearth of accurate assignments for chelate rings" in cyclopalladated compounds and that "as yet, there appears to be no cohesive theoretical or empirical rules to predict the effect(s) of C-metal coordination or chelate ring formation on the ^{13}C chemical shift". The aim of the present work is to rectify these deficiencies by providing definitive ^{13}C NMR assignments for a number of cyclopalladated complexes using one- and two-dimensional NMR techniques.

Results and discussion

For effective comparisons of the NMR spectra of different cyclopalladated compounds it seemed desirable to use common spectral recording conditions (solvent, concentration and temperature) as well as common substitution at the other two sites of coordination of the palladium. For this purpose the chelating acetylacetonate anion was chosen since the resulting complexes are neutral, readily soluble in common organic solvents and the acetylacetonate ligand absorbs at characteristic frequencies well separated from other peaks in both proton and carbon-13 spectra. Furthermore, the acetylacetonate anion is symmetrical and hence geometrical isomers are not formed in the preparation of such complexes.

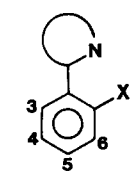
The cyclopalladated complexes of the ligand were prepared by one of two general methods (Scheme 1). The chloro-bridged dimers (**c**) were prepared either by direct treatment of the ligand with lithium tetrachloropalladate or, where this produced only the non-cyclopalladated *trans*-dichloro complex (**d**), by cyclopalladation from palladium acetate, forming the acetate-bridged complex, and then subsequent acetate–chloride exchange. The cyclopalladated acetylacetonate complexes **b** could



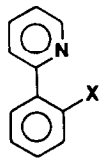
SCHEME 1

then be prepared by anion exchange from the chloro-bridged dimer prepared above. The majority of ligands studied (Scheme 2) had been previously cyclopalladated, though not all of these had been converted to the acetylacetonate complex.

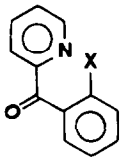
(Continued on p. 108)



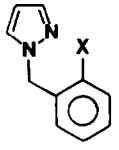
(a) X = H



(1)

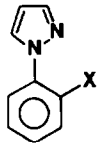


(2)

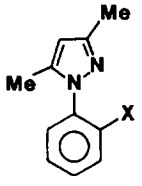


(3)

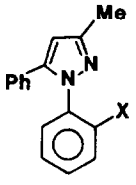
(b) X = Pd(acac)



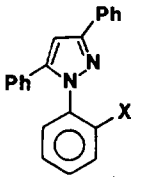
(4)



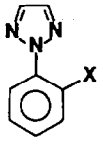
(5)



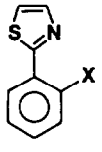
(6)



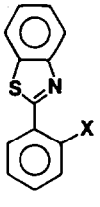
(7)



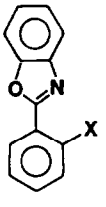
(8)



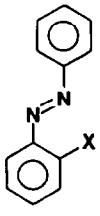
(9)



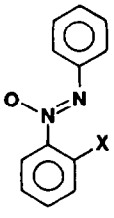
(10)



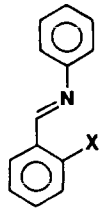
(11)



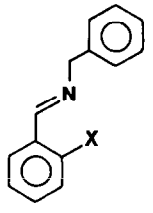
(12)



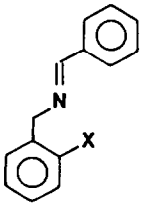
(13)



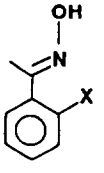
(14)



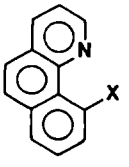
(15)



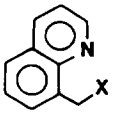
(16)



(17)



(18)



(19)

SCHEME 2

TABLE 1

^{1}H NMR SPECTRA OF THE FREE LIGANDS (a) AND Pd(acac) COMPLEXES (b) ($\Delta = \delta(b) - \delta(a)$)

	H(6)	H(5)	H(4)	H(3)	acac-CH	acac-Me's	Other protons						
1a	7.46	7.39	7.46	7.98			7.68(3′)	7.68(4′)	7.17(5′)	8.67(6′)			
1b	7.60	7.17	7.11	7.42	5.40	2.10, 2.06	7.63	7.79	7.15	8.77			
Δ	+0.14	−0.22	−0.35	−0.56			−0.05	+0.11	−0.02	+0.10			
2a	7.47	7.58	7.47	8.06			8.02(3′)	7.88(4′)	7.47(5′)	8.71(6′)			
2b	7.81	7.52	7.19	7.77	5.44	2.07, 2.02	8.24	8.02	7.55	9.11			
Δ	+0.34	−0.26	−0.28	−0.29			+0.22	+0.14	+0.08	+0.40			
3a	7.33	7.30	7.33	7.20			5.32(CH_2)	7.55(3′)	6.27(4′)	7.37(5′)			
3b	7.52	7.10	7.00	6.96	5.42	2.08, 2.03	5.31	7.84	6.33	7.59			
Δ	+0.19	−0.20	−0.30	−0.24			−0.01	+0.29	+0.06	+0.22			
4a	7.44	7.27	7.44	7.69			7.72(3′)	6.46(4′)	7.92(5′)				
4b	7.55	7.07	7.12	7.06	5.41	2.10, 2.05	7.78	6.45	7.90				
Δ	+0.11	−0.20	−0.32	−0.63			+0.06	−0.01	−0.02				
5a	7.43	7.33	7.43	7.43			5.99(4′)	2.30(3′-Me)	2.29(5′-Me)				
5b	7.60	7.01	7.08	7.13	5.39	2.09, 2.00	5.92	2.54	2.63				
Δ	+0.17	−0.32	−0.35	−0.30			−0.07	+0.24	+0.34				
6a	7.28	7.25	7.28	7.27			6.31(4′)	2.38(3′-Me)	7.27(5′-*o*)	7.22(5′-*m*)	7.27(5′-*p*)		
6b	7.55	6.93	6.74	6.34	5.42	2.10, 2.03	6.10	2.62	7.51	7.45	7.48		
Δ	+0.27	−0.32	−0.54	−0.93			−0.21	+0.24	+0.24	+0.23	+0.21		
7a	7.31	7.28	7.31	7.35			6.82(4′)	7.92(3′-*o*)	7.41(3′-*m*)	7.28(3-*p*)	7.28(5′-*o*)	7.26(5′-*m*)	7.32(5′-*p*)
7b	7.57	6.96	6.76	6.39	5.23	2.03, 1.42	6.40	7.73	7.37	7.39	7.50	7.50	7.52
Δ	+0.26	−0.32	−0.55	−0.96			−0.42	−0.19	−0.04	+0.11	+0.22	+0.24	+0.20
8a	7.48	7.35	7.48	8.09			7.81(4′)	7.81(5′)					
8b	7.58	7.18	7.21	7.52	5.44	2.13, 2.06	7.81	7.95					
Δ	+0.10	−0.17	−0.27	−0.57			0	+0.14					
9a	7.45	7.45	7.45	7.95			7.93(4′)	7.35(5′)					
9b	7.58	7.17	7.09	7.36	5.41	2.10, 2.05	7.87	7.23					
Δ	+0.13	−0.28	−0.36	−0.59			−0.06	−0.12					

10a	7.49	7.49	7.49	8.10			8.08(4′)	7.49(5′)	7.38(6′)	7.90(7′)			
10b	7.65	7.21	7.13	7.44	5.46	2.14, 2.13	9.04	7.53	7.41	7.82			
Δ	+0.16	−0.28	−0.36	−0.66			+0.96	+0.04	+0.03	−0.08			
11a	7.53	7.53	7.53	8.26			7.78(4′)	7.35(5′)	7.35(6′)	7.59(7′)			
11b	7.65	7.27	7.15	7.54	5.45	2.12, 2.12	8.11	7.42	7.37	7.58			
Δ	+0.12	−0.26	−0.38	−0.72			+0.33	+0.07	+0.02	−0.01			
12a	7.49	7.44	7.49	7.92			7.92(*o*)	7.49(*m*)	7.44(*p*)				
12b	7.60	7.28	7.26	7.93	5.42	2.11, 2.00	8.03	7.47	7.48				
Δ	+0.11	−0.16	−0.23	+0.01			+0.11	−0.02	+0.04				
13a	7.51	7.56	7.51	8.32			8.19(*o*)	7.50(*m*)	7.40(*p*)				
13b	7.73	7.42	7.22	7.59	5.36	2.11, 1.82	7.55	7.48	7.40				
Δ	+0.22	−0.14	−0.29	−0.73			−0.64	−0.02	0				
14a	7.47	7.47	7.47	7.90			8.45(CH)	7.21(*o*)	7.39(*m*)	7.22(*p*)			
14b	7.62	7.23	7.10	7.39	5.35	2.09, 1.86	8.13	7.42	7.40	7.34			
Δ	+0.15	−0.24	−0.37	−0.51			−0.32	+0.21	+0.01	+0.12			
15a	7.41	7.41	7.41	7.78			8.39(CH)	4.82(CH_2)	7.34(*o*)	7.34(*m*)	7.27(*p*)		
15b	7.51	7.20	7.02	7.21	5.36	2.06, 1.97	7.89	4.88	7.41	7.35	7.30		
Δ	+0.10	−0.21	−0.39	−0.57			−0.50	+0.06	+0.07	+0.01	+0.03		
16a	7.34	7.27	7.34	7.34			4.82(CH_2)	8.39(CH)	7.78(*o*)	7.41(*m*)	7.41(*p*)		
16b	7.40	7.06	7.06	6.98	5.23	2.04, 1.46	5.16	8.49	8.34	7.39	7.49		
Δ	+0.06	−0.21	−0.28	−0.36			+0.34	+0.10	+0.56	−0.02	+0.08		
17a	7.38	7.38	7.38	7.62			2.31(Me)						
17b	7.42	7.13	7.06	7.10	5.38	2.10, 2.02	2.28						
Δ	+0.04	−0.25	−0.32	−0.52			−0.03						
18a	7.74	7.68	7.89				8.99(2)	7.50(3)	8.14(4)	7.65(5)	7.79(6)	9.30(10)	
18b	7.70	7.51	7.56		5.44	2.15, 2.10	8.86	7.41	8.18	7.49	7.70		
Δ	−0.04	−0.17	−0.33				−0.13	−0.09	+0.04	−0.16	−0.09		
19a							2.83(Me)	8.94(2)	7.38(3)	8.11(4)	7.65(5)	7.42(6)	7.55(7)
19b							3.60(CH_2)	8.95	7.40	8.24	7.56	7.47	7.60
Δ							+0.77	+0.01	+0.02	+0.13	−0.09	+0.05	+0.05

TABLE 2

^{13}C NMR SPECTRA OF THE FREE LIGANDS (a) AND THE Pd(acac) COMPLEXES (b) ($\Delta = \delta(b) - \delta(a)$)

	C(6)	C(5)	C(4)	C(3)	acac	Other carbons						
1a	128.6	128.8	128.6	126.8	Me: 28.1, 27.7	120.4(3′)	136.6(4′)	122.0(5′)	149.5(6′)			
1b	131.4	129.1	124.6	122.8	CO: 188.3, 187.0	118.3	138.4	121.6	148.3			
Δ	+2.8	+0.2	−4.0	−4.0	CH: 100.6	−2.1	+1.8	−0.4	−1.2			
2a	128.1	132.9	128.1	130.9	Me: 28.0, 27.7	124.6(3′)	137.0(4′)	126.1(5′)	148.5(6′)			
2b	128.4	131.1	125.0	134.2	CO: 188.4, 187.1	125.8	138.9	127.2	151.2			
Δ	+0.3	−1.8	−3.1	+3.3	CH: 100.5	+1.2	+1.9	+1.1	+2.7			
3a	128.8	128.0	128.8	127.6	Me: 28.0, 27.7	55.9(CH_2)	139.5(3′)	106.0(4′)	129.2(5′)			
3b	134.2	126.8	124.2	125.1	CO: 188.1, 186.6	58.7	140.9	106.6	131.0			
Δ	+5.4	−1.2	−4.6	−2.5	CH: 100.3	+2.8	+1.4	+0.6	+1.8			
4a	129.4	126.4	129.4	119.2	Me: 27.8, 27.5	141.0(3′)	107.6(4′)	126.7(5′)				
4b	132.0	125.1	124.9	110.5	CO: 188.3, 186.4	138.7	106.5	124.8				
Δ	+2.6	−1.3	−4.5	−8.7	CH: 100.5	−2.3	−1.1	−1.9				
5a	128.9	127.2	128.9	124.7	Me: 27.6, 27.6	106.9(4′)	13.4(3′-Me)	12.3(5′-Me)				
5b	131.5	123.8	124.8	111.5	CO: 187.9, 186.3	109.1	12.0	14.1				
Δ	+2.6	−3.4	−4.1	−13.2	CH: 99.9	+2.2	−1.4	+1.8				
6a	128.8	127.0	128.8	125.1	Me: 27.6, 27.6	107.7(4′)	13.5(3′-Me)	128.3(5′-*o*)	128.6(5′-*m*)	128.0(5′-*p*)		
6b	131.2	124.0	124.3	112.7	CO: 187.9, 186.3	109.9	12.1	128.9	129.4	129.7		
Δ	+2.4	−3.0	−4.5	−12.4	CH: 100.0	+2.2	−1.4	+0.6	+0.8	+1.7		
7a	128.9	127.4	128.9	125.3	Me: 27.3, 26.9	102.0(4′)	125.8(3′-*o*)	128.6(3′-*m*)	128.3(3′-*p*)	128.5(5′-*o*)	128.7(5′-*m*)	128.0(5-*p*)
7b	131.4	124.5	124.3	113.4	CO: 187.7, 185.4	109.6	129.7	127.6	128.9	129.4	129.0	129.9
Δ	+2.5	−2.9	−4.6	−11.9	CH: 99.8	+7.6	+3.9	−1.0	+0.6	+0.9	+0.3	+1.9
8a	129.3	127.5	129.3	118.9	Me: 27.7, 27.4	135.5(4′)	135.5(5′)					
8b	131.4	126.8	125.5	113.6	CO: 188.5, 186.4	134.0	133.2					
Δ	+2.1	−1.3	−3.8	−5.3	CH: 100.7	−1.5	−2.2					
9a	129.1	130.4	129.1	126.8	Me: 27.9, 27.6	143.2(4′)	119.0					
9b	131.1	129.0	124.7	122.9	CO: 188.2, 186.5	139.5	115.6					
Δ	+2.0	−1.4	−4.4	−3.9	CH: 100.6	−3.7	−3.4					

10a	129.0	131.0	129.0	127.6	Me: 27.9, 27.6	123.3(4′)	126.3(5′)	125.2(6′)	121.6(7′)			
10b	130.9	130.6	124.9	124.4	CO: 188.0, 186.4	121.5	127.4	125.5	121.9			
Δ	+1.9	−0.4	−4.1	−3.2	CH: 100.3	−1.8	+1.1	+0.3	+0.3			
11a	128.9	131.5	128.9	127.6	Me: 27.7, 27.5	120.0(4′)	125.1(5′)	124.6(6′)	110.6(7′)			
11b	130.9	131.0	124.8	124.4	CO: 188.8, 188.0	117.9	126.0	125.3	111.2			
Δ	+2.0	−0.5	−4.1	−3.2	CH: 100.3	−2.1	+0.9	+0.7	+0.6			
12a	129.1	131.0	129.1	122.9	Me: 28.1, 27.6	122.9(*o*)	129.1(*m*)	131.0(*p*)				
12b	131.5	131.2	125.7	128.8	CO: 188.7, 186.4	124.1	128.3	130.9				
Δ	+2.4	+0.2	−3.4	+5.9	CH: 100.4	+1.2	−0.8	−0.1				
13a	128.8	131.6	128.8	122.4	Me: 27.6, 27.2	125.3(*o*)	128.7(*m*)	129.6(*p*)				
13b	130.7	132.7	125.3	121.5	CO: 188.7, 185.9	125.5	128.1	129.2				
Δ	+1.9	+1.1	−3.5	−0.9	CH: 100.4	+0.2	−0.6	−0.4				
14a	128.8	131.4	128.8	128.8	Me: 27.9, 27.4	160.4(CH)	120.9(*o*)	129.1(*m*)	125.9(*p*)			
14b	130.9	130.5	124.6	127.9	CO: 188.4, 185.9	174.4	123.4	128.5	127.8			
Δ	+2.1	−0.9	−4.2	−0.9	CH: 100.2	+14.0	+2.5	−0.6	+1.9			
15a	128.6	130.7	128.6	128.3	Me: 27.9, 27.5	162.0(CH)	65.0(CH_2)	128.0(*o*)	128.5(*m*)	127.0(*p*)		
15b	130.9	129.8	124.2	126.8	CO: 188.1, 186.4	174.7	60.6	129.0	128.7	127.8		
Δ	+2.3	−0.9	−4.4	−1.5	CH: 100.4	+12.7	−4.4	+1.0	+0.2	+0.8		
16a	128.5	127.0	128.5	128.0	Me: 27.6; 27.5	65.0(CH_2)	162.0(CH)	128.3(*o*)	128.6(*m*)	130.7(*p*)		
16b	130.6	125.1	124.7	119.8	CO: 187.3, 186.4	74.0	167.9	129.9	127.7	132.1		
Δ	+2.1	−1.9	−3.8	−8.2	CH: 99.7	+9.0	+5.9	+1.6	−0.9	+1.4		
17a	128.5	129.3	128.5	126.1	Me: 27.9, 27.7	12.4(Me)						
17b	130.4	128.6	124.5	124.6	CO: 188.4, 187.2	10.8						
Δ	+1.9	−0.7	−4.0	−1.5	CH: 101.1	−1.6						
18a	127.1	128.2	127.8		Me: 28.2, 27.6	148.8(2)	121.8(3)	135.8(4)	125.3(5)	127.8(6)	124.4(10)	
18b	128.9	122.4	122.8		CO: 188.2, 186.7	146.9	120.7	136.7	128.3	129.0		
Δ	+1.8	−5.8	−5.0		CH: 100.6	−1.9	−1.1	+0.9	+3.0	+1.2		
19a					Me: 28.5, 27.5	18.2(CH_3)	149.3(2)	120.8(3)	136.3(4)	125.9(5)	126.3(6)	129.6(7)
19b					CO: 188.2, 187.2	22.3(CH_2)	147.8	121.0	137.3	123.1	128.2	128.7
Δ					CH: 100.0	+4.1	−1.5	+0.2	+1.0	−2.8	+1.9	−0.9

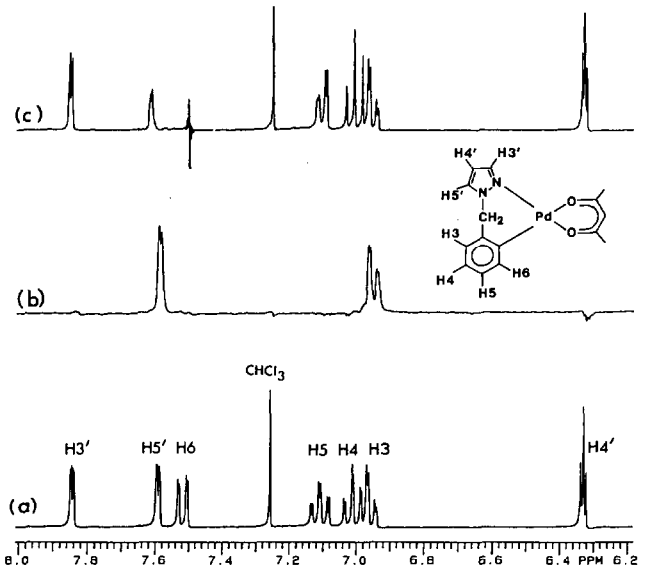


Fig. 1. Proton NMR spectra of **3b**.

Tables 1 and 2 list the assigned ^{1}H and ^{13}C NMR spectra respectively for the ligand LH (**a**) and [PdL(acac)] complex (**b**) along with chemical shift differences $\Delta = \delta(\mathbf{b})-\delta(\mathbf{a})$.

The general procedure for assigning these spectra was as follows. Firstly, ^{1}H NMR spectra were tentatively assigned on the basis of chemical shift and spin–spin coupling information. The assignments were then unambiguously confirmed by a variety of techniques, where appropriate, using selective proton decoupling, difference NOE [25] or two-dimensional homonuclear correlation spectroscopy (COSY) [26] experiments.

Figure 1 shows a typical example. Figure 1(a) shows the aromatic region of the normal ^{1}H NMR spectrum of the cyclopalladated acetylacetonate complex **3b** of 1-benzylpyrazole. Inspection of the spin–spin coupling displayed by these protons identifies the two doublets of the terminal pyrazole protons (H(3′), H(5′)) at (7.85, 7.59 ppm) coupled to the triplet of the middle pyrazole proton H(4′) at 6.33 ppm. The remaining two doublets of doublets and two triplets of doublets correspond to the two terminal phenyl protons (H(3), H(6)) and two central phenyl protons (H(4), H(5)). However, distinction within each pair is not possible from just this spectrum alone.

Figure 1(b) shows the difference NOE spectrum obtained by irradiation of the benzylic methylene protons at 5.31 ppm. The significant enhancements of the signals at 7.59 (12%) and 6.96 ppm (13%) identifies these signals as being from the protons H(5′) and H(3) respectively, closest in space to the methylene being irradiated. Hence by elimination the remaining doublet of doublets at 7.52 ppm must be due to H(6). Figure 1(c) shows the spectrum resulting from homonuclear irradiation of this latter signal. The triplet of doublets at 7.10 ppm collapses to a doublet of doublets, whilst the long range (^{4}J(H–H)) coupling is lost from the triplet of doublets at 7.00 ppm thereby identifying these signals as being due to a

proton *ortho* and *meta* to that being irradiated; that is H(5) and H(4) respectively, and thus completing the ^{1}H NMR assignment.

Figure 2(a) shows a contour plot of the COSY [26] spectrum of the cyclopalladated acetylacetonate complex of 2-benzoylpyridine (**2b**) and includes the normal (1D) spectrum plotted above for comparison. The four protons in each ring are immediately distinguished by the off-diagonal connectivities as shown. The assignment of the four pyridine ring protons is straightforward from this spectrum because of the low-field position of the proton adjacent to the nitrogen. Assignment of the four phenyl ring protons, however, requires additional (1D) experiments.

Having assigned the ^{1}H NMR spectra, the assignment of the ^{13}C NMR spectra is straightforward by means of heteronuclear 2D correlation spectroscopy [27]. This is exemplified in Fig. 2(b) for the 2-benzoylpyridine complex (**2b**) in which the ^{13}C NMR spectrum on the vertical axis, is assigned from the cross-correlation peaks to

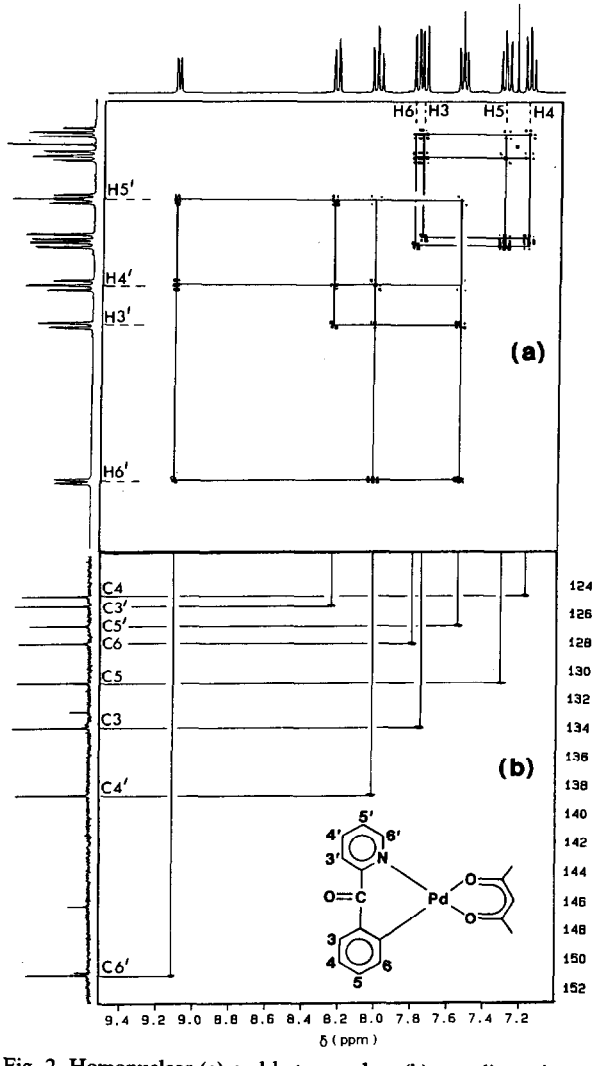


Fig. 2. Homonuclear (a) and heteronuclear (b) two-dimensional correlation spectra of **2b**.

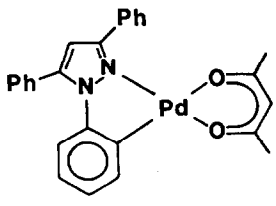
the previously assigned ^1H NMR spectrum, on the horizontal axis.

The ^1H and ^{13}C NMR spectra listed in Tables 1 and 2 were assigned by techniques similar to those described in the above examples for both the cyclopalladated complexes **b** and the free ligands **a**. Assignment of the ^{13}C NMR spectra of the free ligands revealed a number of incorrect assignments in the literature. The reported tentative assignments of two carbons in the pyridine ring of 2-phenylpyridine (**1a**) [28] the *ortho* and *meta* carbons of 2-phenylthiazole (**9a**) [11] and 2-phenylbenzothiazole (**10a**) [29] and the *ortho* and *para* carbons of azoxybenzene (**13a**) [28] were shown to be incorrect. Several assignments for the spectrum of benzo[*h*]quinoline (**18a**) [28] are incorrect and our chemical shift values for 2-phenyl-1,2,3-triazole (**8a**) differ from those previously reported [30]. Our assignments agree with the literature values for 1-benzylpyrazole (**3a**) [30] 1-phenylpyrazole (**4a**) [30,31], 3,5-dimethyl-1-phenylpyrazole (**5a**) [32], 2-phenylbenzoxazole (**11a**) [33], azobenzene (**12a**) [28], *N*-benzylideneaniline (**14a**) [34], *N*-benzylidenebenzylamine (**15a**) [35], *E*-acetophenone oxime (**17a**), [36] and 8-methylquinoline (**19a**) [37]. In the ^{13}C NMR spectra of the cyclopalladated complexes the quaternary peaks were not assigned.

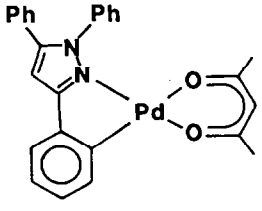
The observed downfield shift of H(6) in the 2-phenylpyridine complex **1b**, relative to the free ligand **1a**, contrasts with an upfield shift in the corresponding acetato complex due to through-space interactions of overlying aromatic rings [38]. Furthermore both the ^1H and ^{13}C NMR chemical shifts of the complex **1b** differ significantly from previously reported cyclometallated complexes of Rh^{III}, Ir^{III}, [39] and Ru^{II} [23,24] with the same ligand. These differences can be explained by through-space interligand effects operating in these octahedral complexes but absent in the square-planar palladium complex **1b**. The ^1H NMR spectrum of the 2-benzoylpyridine complex **2b** has been previously reported without assignments [13]. Our chemical shift values are in generally good agreement except for the shift of the C(3) pyridine proton at 8.24 ppm, differing from the previously reported value of 8.82 ppm.

The previously reported [40] assignments of the H(3), H(6), H(3′), H(5′) protons of the 1-phenylpyrazole complex **4b** were shown to be in error by means of difference NOE and heteronuclear correlated 2D spectra, as well as a consideration of the magnitude of the coupling constants.

The ^1H NMR spectrum of the 1,5-diphenyl-3-methylpyrazole derivative **6b** showed larged upfield shifts of the protons in the palladated phenyl ring. An X-ray crystal structure [41] of this compound shows that the C(5)-phenyl ring is in a conformation approximately orthogonal to the cyclopalladated phenyl ring. Thus the upfield shifts are attributed to these protons lying in the shielding region above the C(5)-phenyl ring. Since 1,3,5-triphenylpyrazole possesses two phenyl rings suitably located for metallation, two products **7b** and **7e** could result from the



(7b)



(7e)

cyclopalladation reaction. The upfield shifts of the palladated phenyl ring protons and the close similarity of the NMR spectra to those of **6b** clearly indicate that the N(1)-phenyl group has been metallated, i.e. product **7b** is produced. Furthermore, the relative high field position (1.42 ppm) of one of the acetylacetone methyl groups indicates that the C(3)-phenyl group also lies approximately orthogonal to the pyrazole ring such that the *cis* methyl group lies above the shielding plane of this phenyl ring.

The ^{1}H and ^{13}C NMR spectra of the cyclopalladated phenyl heterocycles **8b–11b** are relatively straightforwardly assigned by methods similar to those described above. The ^{1}H NMR (100 MHz) spectrum of **9b** has been previously reported [11] and the phenyl ring protons described as "complicated multiplets". However at 300 MHz these were clearly resolved and readily assigned. The proton NMR chemical shifts of the aromatic protons in the 2-phenylbenzothiazole and -benzoxazole complexes, **10b** and **11b** respectively, differ markedly from those previously reported for the related 2-*p*-tolyl-cyclopalladated acetate-bridged dimers. The highfield shifts observed in the dimers are attributed to mutual shielding between the planar ligands which have been shown by X-ray crystallography to lie parallel to one another [42]. It has been previously observed that the proton chemical shifts of cyclopalladated arylazonaphthalenes are strongly dependent on the nature of additional ligands coordinated to the palladium [14].

The proton NMR spectra of the complexes **12b** and **13b**, of azobenzene and azoxybenzene are similar to those of related compounds [43]. The ^{13}C NMR spectrum of **12b** has been previously reported without asssignments. The ^{13}C chemical shfts of **12b** differ markedly from those for previously reported cyclomercurated and cyclotellurated complexes of azobenzene [44] which emphasises the influence of the metal on the carbon chemical shifts.

The proton NMR spectrum of **14b** has been previously reported without assignment of the aromatic protons [45]. The ^{1}H NMR spectrum of **14b** again differs markedly from that of the acetate-bridged dimer of cyclopalladated *N*-benzylidene-*p*-toluidine [16] due to mutual interligand shielding in the latter case. This is in contrast to the ^{13}C NMR spectra which are similar. The carbon spectra of the complexes **18b** and **19b** have been previously reported but without assignment of the aromatic carbons [9].

Conclusion

For those metallocycles where a five-membered ring has been formed on cyclopalladation of a phenyl group, inspection of the changes in chemical shift induced by the Pd(acac) group shows some consistent patterns. For protons H(6), H(5) and H(4) the following shifts are observed (standard deviation in parentheses): Δ +0.14 (0.06), −0.24 (0.06) and −0.36 (0.09) respectively. Similarly, carbons C(6), C(5) and C(4) show the following shifts on cyclopalladation: +2.2 (0.3), −1.2 (1.2) and −4.2 (0.4) respectively. The relatively large upfield shift of C(4), *para* to the Pd atom and unaffected by steric interactions, clearly indicates the existence of some metal-to-ligand back-bonding [38], a conclusion supported by X-ray data [41]. In contrast to the above consistent shifts both H(3) and C(3) show large variations in the change in chemical shift resulting from cyclopalladation. The often large effects experienced by H(3) and C(3) can be attributed to changes in conformation which occur within

the ligand on cyclometallation. For example, large upfield shifts are experienced by C(3) in cases where strong steric interactions exist in the complex, in which the rings are obligatorily coplanar, but which do not exist in the free ligand. Chemical shift changes elsewhere in the ligands appear also to be irregular.

Although consistent substituent effects are observed in the present series of compounds it should be noted that these apply only to the Pd(acac) substituent. Thus comparison with previously reported spectra of cyclopalladated compounds in which the acetylacetonate ligand is replaced by other ligands (halide, acetate, pyridines, phosphines, etc.) shows significant deviations from both our ^{13}C and ^{1}H NMR values. For example, aromatic ligands (eg. pyridine, triphenylphosphine) induce large upfield shifts in proton spectra due to through space effects. Furthermore comparison of the spectra of cyclopalladated compounds with those of other cyclometallated compounds shows marked differences due to both electronic and steric effects, especially when compared to cyclometallated compounds with octahedral coordination geometry.

Experimental

All NMR spectra were recorded using a Varian XL-300 spectrometer equipped with a 5 mm switchable probe operating at 299.930 and 75.426 MHz for ^{1}H and ^{13}C respectively. Spectra were recorded at 23°C on ca. 2% (w/v) solutions in $CDCl_3$ with $SiMe_4$ as internal standard. Difference NOE spectra were obtained in an arrayed experiment with the decoupler offset 10,000 Hz and then cycled over the multiplet peaks of the desired proton for irradiation, using a procedure based on that of Kinns and Sanders [46]. The resultant FIDs were then subtracted and transformed. COSY spectra were recorded in the normal fashion using the well established pulse sequence and phase cycling of Bax, Freeman and Morris [26]. Typically 128 t_1 increments were employed and after Fourier transformation the final 512 × 512 spectrum was symmetrized prior to contour plotting. Heteronuclear proton–carbon correlated spectra were recorded in the usual manner [27], typically as a 128 × 1K matrix.

Commercial samples of **1a, 2a, 12a, 13a, 18a** and **19a** were used. The following ligands were prepared by the literature procedure: **3a–7a** [41], **8a** [47], **9a** [48], **10a** [49], **11a** [50], **14a** [51], **15a** [52], **17a** [53].

Preparation of complexes

(a) Chloro-bridged dimers. These were prepared either directly by reaction of the ligand with lithium tetrachloropalladate or by reaction with palladium acetate and subsequent acetate halide exchange, according to the following literature procedures: **1c** [54], **2c** [13], **3c–7c** [41], **8c** [55], **9c** [11], **12c** [1], **13c** [56], **14c** [45], **17c** [53], **18c**, **19c** [57].

(b) Acetylacetonate complexes. The chloro-bridged dimers were converted into the acetylacetonate monomers as described in ref. 41. The following complexes have been previously reported: **2b** [13], **3b–7b** [41], **9b** [11], **12b** [58], **14b** [45], **18b** [9,59], **19b** [9]. The following have not been previously reported:

*Acetylacetonato[2-(2-pyridyl)phenyl-C^1,$N^{1'}$]palladium(II) (**1b**)*, m.p. 236°C (dec). Found: C, 53.3; H, 4.2; N, 3.9. $C_{16}H_{15}NO_2Pd$ calc: C, 53.4; H, 4.2; N, 3.9%.

*Acetylacetonato[2-(1,2,3-triazol-2-yl)phenyl-C^1,$N^{2'}$)palladium(II) (**8b**)*, m.p. 165°C. Found: C, 44.9; H, 3.8; N, 12.0. $C_{13}H_{13}N_3O_2Pd$ calc: C, 44.7; H, 3.8; N, 12.1%.

Acetylacetonato[2-(benzothiazol-2-yl)phenyl-C^1,$N^{3'}$]palladium(II) ***(10b)***, m.p. 247 °C (dec). Found: C, 51.2; H, 3.6; N, 3.2. $C_{18}H_{15}NO_2SPd$ calc: C, 52.0; H, 3.6; N, 3.4%.

Acetylacetonato[2-(benzoxazol-2-yl)phenyl-C^1,$N^{3'}$]palladium(II) ***(11b)***, m.p. 220 °C (dec). Found: C, 52.5; H, 3.6; N, 3.6. $C_{18}H_{15}NO_3Pd$ calc: C, 54.1; H, 3.8; N, 3.5%.

Acetylacetonato[2-(phenyl-NNO-azoxy)phenyl-C^1,$N^{1'}$]palladium(II) ***(13b)***, m.p. 201 °C. Found: C, 50.7; H, 4.1; N, 7.0. $C_{17}H_{16}N_2O_3Pd$ calc: C, 50.7; H, 4.0; N, 7.0%.

Acetylacetonato[2-(acetohydroximoyl)phenyl-C^1,N^1]palladium(II) ***(17b)***, m.p. 183–185 °C (dec). Found: C, 45.8; H, 4.4; N, 4.1. $C_{13}H_{15}NO_3Pd$ calc: C, 46.0; H, 4.5; N, 4.1%.

Acknowledgement

We wish to thank the Research Committee of the New Zealand Universities Grants Committee for funds for the purchase of instrumentation, Dr S.F. Dyke for the gift of samples of **15b** and **16b** and, especially, Dr J.W. Blunt for invaluable discussions and advice.

Reference

1 A.C. Cope and R.W. Siekman, J. Am. Chem. Soc., 87 (1965) 3272.
2 I. Omae, J. Organomet. Chem. Library, 18 (1986) 35.
3 E.C. Constable, Polyhedron, 3 (1984) 1037.
4 G.R. Newkome, W.E. Puckett, V.K. Gupta and G.E. Kiefer, Chem. Rev., 86 (1986) 451.
5 J. Dehand and M. Pfeffer, Coord. Chem. Rev., 18 (1976) 327.
6 N. Barr and S.F. Dyke, J. Organomet. Chem., 243 (1983) 223.
7 A.D. Ryabov, Synthesis, (1985) 233.
8 B.E. Mann and B.F. Taylor, ^{13}C NMR Data for Organometallic Compounds, Academic Press, London, 1981.
9 A.R. Garber, P.E. Garrou, G.E. Hartwell, M.J. Smas, J.R. Wilkinson and L.J. Todd, J. Organomet. Chem., 86 (1975) 219.
10 J. Dehand, C. Mutet and M. Pfeffer, J. Organomet. Chem., 209 (1981) 255.
11 K. Hiraki, Y. Fuchita and S. Takakura, J. Organomet. Chem., 210 (1981) 273.
12 H. van der Poel and G. van Koten, J. Organomet. Chem., 217 (1981) 129.
13 Y. Fuchita, K. Hiraki and Y. Kage, Bull. Chem. Soc. Japan, 55 (1982) 955.
14 A.J. Klaus and P. Rys, Helv. Chim. Acta, 64 (1981) 1452.
15 N. Barr, S.F. Dyke and R.L.W. Frost, Org. Magn. Reson., 22 (1984) 277.
16 P.S. Pregosin and R. Ruedi, J. Organomet. Chem., 273 (1984) 401.
17 P.W. Clark and S.F. Dyke, J. Organomet. Chem., 276 (1984) 421.
18 P.W. Clark and S.F. Dyke, J. Organomet. Chem., 281 (1985) 389.
19 A.A. Watson, D.A. House and P.J. Steel, J. Organomet. Chem., 311 (1986) 387.
20 G.A. Morris, Mag. Reson. Chem., 24 (1986) 371.
21 R. Benn and H. Gunther, Angew. Chem. Int. Ed. Engl., 22 (1983) 350.
22 P. Reveco, J.H. Medley, A.R. Garber, N.S. Bhacca and J. Selbin, Inorg. Chem., 24 (1985) 1096.
23 P. Reveco, W.R. Cherry, J. Medley, A. Garber, R.J. Gale and J. Selbin, Inorg. Chem,., 25 (1986) 1842.
24 E.C. Constable and J.M. Holmes, J. Organomet. Chem., 301 (1986) 203.
25 J.K.M. Sanders and J.D. Mersh in J.W. Emsley, J. Freeney and L.H. Sutcliffe (Eds.), Prog. Nucl. Magn. Reson. Spectrosc., Pergamon Press, Oxford, 15 (1983) 353.
26 A. Bax, R. Freeman and G. Morris, J. Magn. Reson., 42 (1981) 164.
27 A. Bax and G.A. Morris, J. Magn. Reson., 42 (1981) 501.
28 Sadtler Standard NMR Spectra, Sadtler Research Laboratories, Philadelphia.

29 J. Perregaard and S.O. Lawesson, Acta Chem. Scand., B31 (1977) 203.
30 M. Begtrup, Acta Chem. Scand., 27 (1973) 3101.
31 G.E. Hawkes, E.W. Randall, J. Elguero and C.J. Marzin, J. Chem. Soc., Perkin Trans. 2, (1977) 1024.
32 E. Gonzalez, R. Faure, E.J. Vincent, M. Espada and J. Elguero, Org. Magn. Reson., 12 (1979) 587.
33 J. Llinares, J.P. Galy, R. Faure, E.J. Vincent and J. Elguero, Can. J. Chem., 57 (1979) 937.
34 T. Axenrod, X.H. Huang, M.J. Wieder and C.M. Watnick, Magn. Reson. Chem., 24 (1986) 274.
35 J.E. Arrowsmith, M.J. Cook and D.J. Hardstone, Org. Magn. Reson., 11 (1978) 160.
36 G.W. Buchanan and B.A. Dawson, Can. J. Chem., 56 (1978) 2200.
37 P.A. Claret and A.G. Osborne, Org. Magn. Reson., 8 (1976) 147.
38 M.A. Gutierrez, G.R. Newkome and J. Selbin, J. Organomet. Chem., 202 (1980) 341.
39 S. Sprouse, K.A. King, P.J. Spellane and R.J. Watts, Inorg. Chem., 106 (1984) 6647.
40 M. Nonoyama and H. Takayanagi, Trans. Met. Chem., 1 (1975) 10.
41 G.B. Caygill and P.J. Steel, J. Organomet. Chem., 327 (1987) 115.
42 M.R. Churchill, H.J. Wasserman and G.J. Young, Inorg. Chem., 19 (1980) 762.
43 A.K. Mahapatra, D. Bandyopadhyay, P. Bandyopadhyay and A. Chakravorty, Inorg. Chem., 25 (1986) 2214.
44 M.A.K. Ahmed, W.R. McWhinnie and T.A. Hamor, J. Organomet. Chem., 281 (1985) 205.
45 H. Onoue and I. Moritani, J. Organomet. Chem., 43 (1972) 431.
46 M. Kinns and J.K.M. Sanders, J. Magn. Reson., 56 (1984) 518.
47 J.L. Riebsomer, J. Org. Chem., 13 (1948) 815.
48 D.S. Noyce and S.A. Fike, J. Org. Chem., 38 (1973) 2433.
49 M.T. Bogert and E.M. Abrahamson, J. Am. Chem. Soc., 44 (1922) 826.
50 B. Despax, N. Paillous, A. Lattes and A. Paillous, J. Appl. Polym. Sci., 27 (1982) 225.
51 L.A. Bigelow and H. Eatough, Org. Syntheses, Coll. Vol. I, (1932) 80.
52 P.A.S. Smith and C. Van Dang, J. Org. Chem., 41 (1976) 2013.
53 H. Onoue, K. Minami and K. Nakagawa, Bull. Chem. Soc. Japan, 43 (1970) 3480.
54 A. Kasahara, Bull. Chem. Soc. Japan, 41 (1968) 1272.
55 J.A.C. Allison, H.S. El Khadem and C.A. Wilson, J. Heterocycl. Chem., 12 (1975) 1275.
56 A.L. Balch and D. Petridis, Inorg. Chem., 8 (1969) 2247.
57 G.E. Hartwell, R.V. Lawrence and M.J. Smas, J. Chem. Soc., Chem. Commun., (1970) 912.
58 R.F. Heck, J. Am. Chem. Soc., 90 (1968) 313.
59 B.N. Cockburn, D.V. Howe, T. Keating, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1973) 404.