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APPLICATION OF ^{13}C NMR TO THE DETERMINATION OF METAL—CARBON σ BOND FORMATION IN CYCLOMETALLATION REACTIONS WITH NITROGEN DONOR LIGANDS

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Summary

A series of cyclometallated complexes of the nitrogen donor ligands, azobenzene, *N,N*-dimethylbenzylamine, 8-methylquinoline, and benzo[*h*]-quinoline have been examined by ^{13}C NMR. The total number of expected aromatic quaternary and CH carbon atom resonances were determined by comparison of the noise decoupled and single frequency off resonance decoupled spectra of a given complex. In this manner it can be readily determined that cyclometallation may have occurred. In those cases where metal—^{13}C coupling is observed an unambiguous determination of metal—carbon σ bond formation is achieved.

Introduction

In recent years considerable interest has developed concerning the formation of metal—carbon σ bonds by intramolecular proton abstraction [1]. The large variety of ligands which have been reported to undergo the cyclometallation reaction include phosphorus [2], nitrogen [3], sulfur [4], and oxygen [5] compounds having aromatic carbon to metal bonds as well as phosphorus [6] and nitrogen [7] compounds with aliphatic carbon to metal bonds. A proton NMR spectrum can be used to verify the formation of an aliphatic carbon to metal bond [6, 7]. This is done by comparing the integrated area of the CH_2—metal resonance to the area of other proton resonances in the molecule. In certain cases these relative areas do not give a clear-cut answer. The proton NMR spectra of cyclometallation products having aromatic carbon to metal bonds are usually very complicated and an X-ray structure study is required to confirm the formation of a metal—carbon σ bond [8, 9]. The substantial strength of ^{13}C NMR as a structural tool in organometallic chemistry

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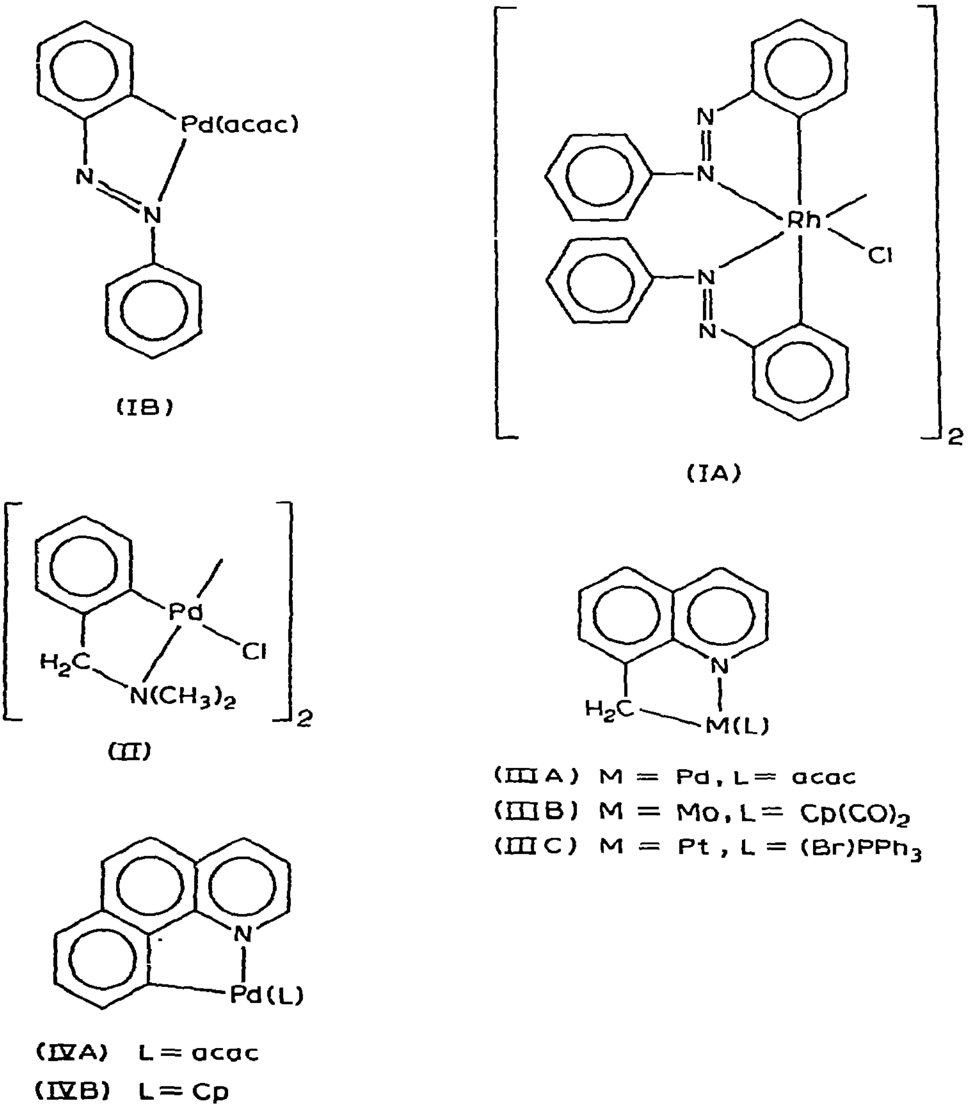
is rapidly becoming apparent [10, 11]. We have examined the ^{13}C NMR spectra of several cyclometallated nitrogen donor complexes having either aliphatic or aromatic carbon to metal bonds to determine whether this structural tool would be useful for identification of the formation of carbon—metal σ bonds.

Results and discussion

The two most prevalent classes of ligands known at present to undergo cyclometallation contain either nitrogen or phosphorus donor sites. For this initial study we chose nitrogen donor ligands in order to avoid the added complication of ^{31}P—^{13}C coupling which would make interpretation of the spectra more difficult. We have examined the ^{13}C NMR spectra of the metal complexes shown in Scheme 1. In the examples studied here we were able to determine that a metal—carbon σ bond was present in the structure.

SCHEME 1



(IIIA) M = Pd, L = acac
(IIIB) M = Mo, L = Cp(CO)$_2$
(IIIC) M = Pt, L = (Br)PPh$_3$

(IVA) L = acac
(IVB) L = Cp

Complexes of azobenzene

The proton decoupled ^{13}C NMR spectrum of azobenzene contained four resonances (see Table 1) with relative areas 1/2/2/1 reading upfield. Examination of the spectrum while employing single frequency off resonance decoupling (SFORD), indicated that only the unit area resonance at 152.2 ppm was a quaternary carbon atom which showed no proton spin coupling. The noise decoupled ^{13}C NMR spectrum of the rhodium complex Ia is presented in Fig. 1. This ^{13}C NMR spectrum contains the expected 10 resonances for the cyclometallated structure. These are designated as A through J in Fig. 1 and the corresponding chemical shift values are given in Table 1. The low field doublet centered at 166 ppm is due to the rhodium-substituted carbon atom with $^{103}Rh—^{13}C$ coupling of 37 Hz. Peaks B and C in Fig. 1 are due to the two nitrogen-substituted carbon atoms. Careful examination of peak C indicates that it is a doublet ($^{2}J(RhC)$ 2 Hz) which is probably due to a nitrogen-substituted carbon atom adjacent to the rhodium atom in structure IA.

The ^{13}C NMR spectrum of the palladium complex IB contains the expected 10 phenyl-carbon resonances which are given in Table 1. The three singlet resonances in the cyclometallated structure are observed at 163.8, 157.1 and 151.2 ppm. Some quadrupolar broadening of one of these singlet signals might be possible due to coupling with the ^{105}Pd nuclei (22.2% natural abundance, $I = 5/2$) but no broadening was observed. There are two carbonyl- and two methyl-carbon resonances observed in this spectrum as would be expected of an acetylacetonate group bonded to a square planar palladium(II) complex.

Palladium complex of N,N-dimethylbenzylamine

The ^{13}C NMR spectral data of *N,N*-dimethylbenzylamine are given in Table 1. The four aromatic carbon signals are clearly seen. The quaternary carbon resonance is found at lowest field in the aromatic region. The palladium complex II exhibited a ^{13}C NMR spectrum containing six unit area resonances in the aromatic region. The two lowest field resonances are singlets as indicated by the SFORD measurement. As indicated above in the ^{13}C NMR spectrum of IB, in this spectrum also there was no noticeable quadrupolar broadening of either singlet resonance due to coupling with ^{105}Pd. In the ^{13}C NMR spectra of IA, IB and II the metal-substituted aromatic carbon resonances are spread over a 20 ppm region. In a series of platinum(II) derivatives of the type *trans*-$[(C_6H_5)Pt\{As(CH_3)_3\}_2L]PF_6$, where L is a neutral ligand, the ^{13}C shieldings of the substituted carbon atoms occur over a 28 ppm range [15]. Therefore the metal-substituted aromatic carbon shielding appears to be strongly dependent on the other types of ligands coordinated to the metal and probably will vary over such a range that it will be difficult to pinpoint.

Complexes of 8-methylquinoline

The formation of a methylene carbon to metal σ bond can be ascertained by integration of the proton NMR spectrum. However, this can be somewhat tedious because accurate reproducible peak area measurements are required. Complexes IIIA and IIIB each exhibited in their ^{13}C NMR spectra the expected three quaternary and six CH resonances in the aromatic region. The methylene resonances IIIA and IIIB were readily found as triplet signals in the SFORD

(continued on p. 224)

TABLE 1

^{13}C NMR DATA OF AROMATIC NITROGEN DONOR LIGANDS AND COMPLEXES

Compound	δ(C) (ppm) (relative area)	Assignment
Azobenzene	152.3(1) s^{a}	phenyl carbons
	130.6(2) d	
	128.7(2) d	
	122.5(1) d	
IA^{c}	166.0(1) d (A)^{b}	rhodium-substituted phenyl carbon (^{1}J(Rh—C) 37 Hz)
	162.9(1) s (B)	*N*-substituted phenyl carbon
	152.0(1) d (C)	*N*-substituted phenyl carbon (^{2}J(Rh—C) 2 Hz)
	134.3(1) d (D)	phenyl carbons
	131.4(1) d (E)	
	130.7(1) d (F)	
	130.4(1) d (G)	
	128.1(2) d (H)	
	125.0(2) d (I)	
	124.1(1) d (J)	
IB	188.5(1) s	acac carbonyl carbons
	186.2(1) s	
	163.8(1) s	phenyl carbons
	157.1(1) s	
	151.2(1) s	
	131.4(1) d	
	131.1(1) d	
	130.7(1) d	
	128.6(1) d	
	128.2(2) d	
	125.6(1) d	
	124.1(2) d	
	100.4(1) d	acac methylene carbon
	28.1(1) q	acac methyl carbons
	27.6(1) q	
N,N-Dimethylbenzylamine	138.5(1) s	phenyl carbons
	128.4(2) d	
	127.6(2) d	
	126.4(1) d	
	63.9(1) t	methylene carbon
	44.7(2) q	*N*-methyl carbons
II	146.7(1) s	phenyl carbons
	142.9(1) s	
	133.0(1) d	
	125.0(1) d	
	124.6(1) d	
	121.4(1) d	
	73.1(1) t	methylene carbon
	52.6(2) q	*N*-methyl carbons

(Table continued)

TABLE 1 (continued)

Compound	δ(C) (ppm) (relative area)	Assignment
8-Methylquinoline	148.3(1) d	aromatic carbons
	146.6(1) s	
	136.4(1) s	
	135.3(1) d	
	128.8(1) d	
	127.5(1) s	
	125.5(1) d	
	125.1(1) d	
	120.0(1) d	
	17.6(1) q	methyl carbon
IIIA	187.9(1) s	acac carbonyl carbons
	185.8(1) s	
	153.9(1) s	aromatic carbons
	149.0(1) s	
	147.6(1) d	
	137.2(1) d	
	128.8(1) s	
	128.6(1) d	
	128.0(1) d	
	123.0(1) d	
	120.9(1) d	
	99.9(1) d	acac methylene carbon
	28.5(1) q	acac methyl carbons
	27.5(1) q	
	22.4(1) t	metal-bonded methylene carbon
IIIB	not observed	carbonyl carbons
	150.9(1) s	aromatic carbon atoms
	147.9(1) d	
	145.2(1) s	
	137.5(1) d	
	128.4(1) s	
	127.8(1) d	
	126.4(1) d	
	123.2(1) d	
	120.6(1) d	
	93.2(5) d	C_5H_5 group
	−1.0(1) t	metal-bonded methylene carbon
benzo[*h*]quinoline	148.2(1) d	aromatic carbon atoms
	146.0(1) s	
	135.1(1) d	
	133.1(1) s	
	131.1(1) s	
	127.6(1) d	
	127.3(1) d	
	127.1(1) d	
	126.5(1) d	
	125.8(1) s	
	124.8(1) d	
	124.0(1) d	
	121.2(1) d	

(Table continued)

TABLE 1 (continued)

Compound	δ(C) (ppm) (relative area)	Assignment
IVA	187.9	acac carbonyl carbons
	186.4	
	150.9(1) s	aromatic carbon atoms
	146.7(1) d	
	136.7(1) d	
	132.8(1) s	
	129.83(1) d	
	128.77(2) s and d	
	128.2(1) d	
	126.3(1) s	
	122.6(2) s and d	
	122.2(1) d	
	120.6(1) d	
	100.5	acac methylene carbon
	28.2	acac methyl carbons
	27.7	
IVB	158.8(1) s	aromatic carbon atoms
	153.5(1) d	
	139.0(1) d	
	135.6(1) s	
	135.2(1) d	
	134.5(1) s	
	129.1(1) d	
	127.0(2) s and d	
	122.9(1 or 2) d	
	121.3(1) d	
	120.0(1)	
	95.6(5)	C_5H_5 group

[a] s, singlet; d, doublet; t, triplet; q, quartet as observed in SFORD spectrum. [b] Letter notation for these resonances as given in Fig. 1. [c] The solvent used in this case was $(CD_3)_2CO$. The spectra of all other compounds were obtained in $CDCl_3$ solvent.

spectra at 22.6 and −1.0 ppm, respectively. A large variation (~37 ppm) in the ^{13}C chemical shifts of methyl groups directly bonded to transition metals has been observed previously [10]. Therefore, a similar chemical shift range for σ-bonded methylene carbon resonances would be expected. The ^{13}C NMR spectrum of compound IIIc gave a very complex pattern in the phenyl region due in part to ^{31}P—^{13}C coupling. The methylene resonance was centered at 20.5 ppm ($^1J(^{195}Pt—^{13}C)$ 741 Hz; $^2J(^{31}P—^{13}C)$ 5.5 Hz). Previous work has shown [16] that methyl groups bonded to Pt^{II} exhibit $^1J(^{195}Pt—^{13}C)$ 395-698 Hz. It has also been observed earlier [10] that for complexes of the type *cis*- and *trans*-$(PR_3)_2Pt(CH_3)X$, the $^2J(P—Pt—C)$ coupling between mutually *cis* nuclei is 5-9 Hz and mutually *trans* nuclei is about 104 Hz. On this basis we propose that the triphenylphosphine is *cis* to the methylene group in IIIc.

Complexes of benzo[h]quinoline

The thirteen expected ^{13}C aromatic carbon resonances of the free ligand are readily observed and the four quaternary "carbons" are clearly seen in

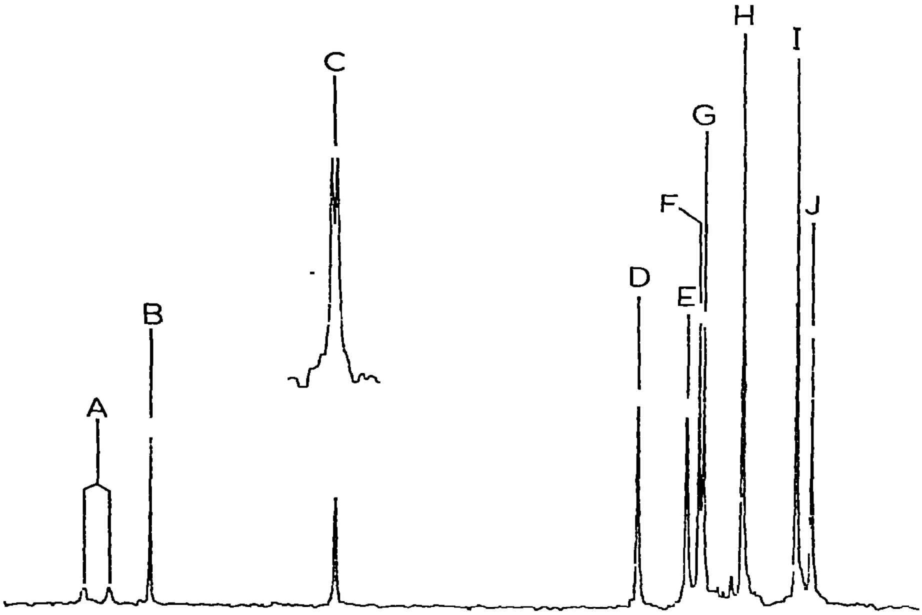


Fig. 1. The noise decoupled ^{13}C NMR spectrum of complex IA.

the SFORD spectrum. In the noise-decoupled spectrum of complex IVA only eleven of the thirteen expected aromatic carbon resonances can be seen. However, the SFORD spectrum of this complex reveals two additional quaternary carbon resonances hidden under the signals at 128.77 and 122.6 ppm. Thus, after observing both noise-decoupled and SFORD spectra, five quaternary and eight CH signals are found in the aromatic carbon region which is consistent with the cyclometallated structure proposed. Careful measurement of the ^{13}C NMR spectra of complex IVB, clearly resolved only 12 of the expected 13 lines. The expected 8 CH resonances were observed but only 4 of the 5 quaternary signals were clearly seen. The additional signal appeared to be at 122.9 ppm but was not clearly resolved after repeated attempts. Use of CD_2Cl_2 as a solvent also did not resolve the problem. Thus it should be borne in mind that while this structural method has its advantages, if the aromatic region of the ^{13}C NMR spectrum is expected to have a large number of signals it may not be possible to clearly see all the resonances.

Experimental section

Instrumentation and ^{13}C NMR procedures

The ^{13}C NMR spectra were obtained at 25.2 MHz with a Varian XL 100-15 instrument. This instrument is equipped with a Transform Technology, Inc. pulse unit which delivers a 90° pulse in 15 μs and 36K Nicholet 1085 computer system with disc. All ^{13}C NMR spectra were measured at 34°C in $CDCl_3$ or acetone-d_6 solvent at a concentration of 0.1 to 0.2 mmol solute per ml solvent. An internal deuterium lock and autoshim were used to maintain high-field homogeneity during acquisition of single frequency off resonance decoupled

(SFORD) spectra. The proton decoupling was accomplished using a Varian Gyrocode decoupler. A noise bandwidth of 700 Hz centered 7 ppm downfield from tetramethylsilane (TMS) was employed for all ^{1}H noise decoupled spectra. For SFORD spectra, the Gyrocode decoupler was operated at 10 Watt in the single-frequency mode and the offset was varied to give the optimum resolution in the crowded phenyl region of the ^{13}C NMR spectrum. An offset of about 17 ppm downfield from TMS was used as the initial setting.

The ^{13}C NMR chemical shift values were measured digitally on 16K or 32K transforms (5000 Hz spectrum width) relative to the internal solvent resonance and are reported in ppm (positive values downfield) from TMS using the conversions $\delta(\text{TMS}) = \delta(\text{CDCl}_3) + 76.98$ ppm and $\delta(\text{TMS}) = \delta[(\text{CD}_3)_2\text{CO}] + 29.22$ ppm. Chemical shift values measured in this manner are probably accurate to within ± 0.04 ppm.

Materials

The compounds dichlorotetrakis[(phenylazo)phenyl-2-*C*,*N*′]dirhodium(I) [12] (compound IA), acetylacetonato[(phenylazo)phenyl-2-*C*,*N*′]palladium(II) [13] (compound IB), and dichlorobis(*N*,*N*-dimethylbenzylamine-2-*C*,*N*)dipalladium(II) [15] (compound II) were prepared by literature procedures.

Pd(Bq)(acac) (Compound IVA)

A solution of benzo[*h*]quinoline (Bq) (1.21 g, 6.76 mmol) in 20 ml of methanol was added to 40 ml of a refluxing aqueous solution containing 6.0 g (3.38 mmol) of Li_2PdCl_4. The resulting yellow precipitate was washed with water to give $[\text{Pd(Bq)Cl}]_2$, (1.05 g, 98%).

A suspension of this dimer (0.64 g, 1 mmol) with sodium methoxide (0.14 g, 2.0 mmol) and 2,4-pentanedione (2 ml) in 30 ml of methanol was stirred overnight before collecting the precipitate. The bright yellow complex Pd(Bq)(acac) was extracted from the precipitate by methylene chloride and crystallized upon concentration of the solution, (0.46 g, 62 %). The complex can be recrystallized from chloroform—hexane, (m.p. 214-215°). Anal. found: C, 57.2; H, 4.11. $\text{C}_{18}\text{H}_{15}\text{NO}_2\text{Pd}$ calcd.: C, 56.4; H, 3.94%.

Pd(Bq)(Cp) (Compound IVB)

To a stirred suspension of $[\text{Pd(Bq)Cl}]_2$, (1.25 g, 2.0 mmol) in 30 ml of tetrahydrofuran was added 8 ml of a 0.5 *M* solution of sodium cyclopentadienide in tetrahydrofuran. A brown-yellow solution quickly developed. The solvent was removed under vacuum and the residue extracted with dichloromethane. Hexane was added to the filtrate which was reduced to ca. 10 ml and large brown-red crystals of Pd(Bq)Cp formed slowly at −20°, (0.38 g, 27%) (m.p. 160° dec.). Anal. found: C, 61.4; H, 3.77. $\text{C}_{18}\text{H}_{13}\text{NPd}$ calcd.: C, 62.0; H, 3.75%.

Pd(Mq)(acac) (Compound IIIA)

The procedure for the preparation of Pd(Bq)(acac) was followed using 8-methylquinoline (Mq), but the initial precipitate is a mixture of $[\text{Pd(Mq)Cl}]_2$ and Pd $(\text{MqH})_2\text{Cl}$.

This mixture (1.0 g,), sodium methoxide (0.200 g, 3.60 mmol) and 2,4-pentanedione (3.5 ml) were stirred for 16 h in methanol (15 ml). The mixture was filtered to remove $Pd(MqH)_2Cl_2$ (0.5 g) and the solvent was removed from the filtrate and the residue extracted with dichloromethane (10 ml). This solution was reduced to 3 ml and hexane (5 ml) was added to produce the bright yellow needles of Pd(Mq)(acac), (0.39 g), (m.p. 194-195°). Anal. found: C, 51.6; H, 4.42. $C_{15}H_{15}NO_2Pd$ calcd.: C, 51.9; H, 4.35%.

PtBr(Mq)(PPH_3) (Compound IIIc)

$Pt(PPh_3)_3$ (0.400 g, 0.408 mmol) and 8-bromomethylquinoline (0.100 g, 0.473 mmol) were refluxed for 2.5 h in toluene (30 ml). The solvent was removed under vacuum, the residue washed with pentane, and then extracted with methylene chloride. The addition of hexane produced bright yellow crystals of $PtBr(Mq)(PPh_3)$ (0.24 g, 85%). Anal. found: C, 48.8; H, 3.61; P, 4.89. $C_{28}H_{23}BrNPPt$ calcd.: C, 49.4; H, 3.42; P, 4.59%.

$Mo(CO)_2$(Mq)(Cp) (Compound IIIB)

A solution of sodium cyclopentadienide (15 mmol) and $Mo(CO)_6$ (3.62 g, 13.7 mmol) in tetrahydrofuran (50 ml) was refluxed for 12 h. After cooling to 0°, 8-bromomethylquinoline (3.0 g, 13.7 mmol) was added and the solution was stirred for 12 h at room temperature. The resulting red-orange solution was concentrated and then eluted through an alumina column by 1/1 ether/hexane. Concentration of the first fraction gave pale orange crystals, which were recrystallized from hexane (0.8 g, 16%), (m.p. 83-85°). Anal. found: C. 56.6; H, 3.48. $C_{17}H_{13}NO_2Mo$ calcd.: C, 56.9; H, 3.62%.

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