A. J. Carty

Phosphorus-31 Nuclear Magnetic Resonance Spectra of Palladium and Platinum Thiocyanate Complexes. Probe of Metal–Thiocyanate Bonding and Novel Source of Phosphorus–Phosphorus and Phosphorus–Nitrogen Coupling Constants

A. J. CARTY

^{31}P NMR spectra have been recorded for the unsymmetrical diphosphine complexes $MX_2(Ph_2PCH_2CCF_3CHPPh_2)$ (M = Pd, Pt; X = Cl, CNS, C^{15}NS). For the chloro complexes with M = Pt, $^2J_{P-P}$ = 19.53 Hz, and with M = Pd, $^2J_{P-P}$ ~ 0. In the spectra of the isotopically substituted complexes, dithiocyanato and mixed thiocyanato–isothiocyanato isomers can be unambiguously identified due to the occurrence of P–P and P–^{15}N coupling. The platinum complexes Pt-(NCS)(SCN)(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) and Pt(SCN)(NCS)(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) also exhibit P–^{14}N coupling between phosphorus nuclei and ^{14}N(I = 1) nuclei in trans isothiocyanate groups. The spectra provide a sensitive and novel probe of thiocyanate bonding modes in solution.

Introduction

Although progress has been made recently toward an understanding of factors influencing the bonding mode of the thiocyanate ion in the solid state,[1] particularly for phosphine complexes[2-4] knowledge of solution equilibria has been hampered by the lack of a probe sufficiently sensitive to unequivocally identify all solution species. Solution infrared spectroscopy,[5] via frequency, bandwidth, and integrated intensity measurements, is capable of providing an indication of whether S, N, or both types of bonding are present[6] but cannot for example differentiate a mixture of square-planar $M(NCS)_2(PR_3)_2$ and $M(SCN)_2(PR_3)_2$ from a mixed species $M(NCS)(SCN)(PR_3)_2$ or indeed distinguish the various isomeric complexes present in a cis–trans mixture of M-$(NCS)_2(PR_3)_2$, $M(SCN)_2(PR_3)_2$, and $M(NCS)(SCN)$-$(PR_3)_2$. For platinum and palladium thiocyanate complexes of phosphites and acetylenic phosphines ^{31}P resonances of thiocyanato, isothiocyanato, and mixed species are chemically shifted from one another and the fortuitous occurrence of ^{14}N–^{31}P coupling in ^{31}P resonances of phosphorus nuclei trans to N-bonded thiocyanate groups facilitates structural identification.[7] Furthermore, valuable ^{31}P–^{31}P and ^{195}Pt–^{31}P coupling constant data can be obtained directly from the spectra of mixed species. In this paper we illustrate the wealth of information available from the ^{31}P spectra of the unsymmetrical diphosphine complexes cis-$M(CNS)_2$-$(Ph_2PCH_2CCF_3CHPPh_2)$ and show that even when ^{14}N–^{31}P coupling is absent in natural abundance spectra, ^{15}N isotopic substitution provides structural data from ^{15}N–^{31}P coupling constants.

Experimental Section

The ligand $Ph_2PC\equiv CCF_3$[8] and the palladium complexes cis-$PdX_2(Ph_2PCH_2CCF_3CHPPh_2)$ (X = Cl, CNS)[9] were synthesized as described in the literature. Potassium tetrachloroplatinate(II) was purchased from Johnson Mathey and Mallory, Toronto, Canada. Sodium thiocyanate (^{15}N) was obtained from Stohler Isotope Chemicals.

cis-$PtCl_2(Ph_2PCH_2CCF_3CHPPh_2)$. The ligand $Ph_2PC\equiv CCF_3$ (1.98 g) was dissolved in absolute ethanol (50 ml) and potassium tetrachloroplatinite (1.48 g) in a minimum of water was added. The aqueous–alcohol mixture, containing precipitated solids, was then stirred at 60 °C for 2 days. The solvent was removed under reduced pressure and the solids were extracted with several portions of dichloromethane. Recrystallization from dichloromethane–ethanol or acetonitrile–methanol afforded good yields (65–70%) of the colorless crystalline complex. Other products of this reaction will be described in detail elsewhere.[10] The same compound can be obtained in somewhat smaller (50–60%) yields by hydrolyzing the cis complex $PtCl_2(Ph_2PC\equiv CCF_2)_2$ in aqueous ethanol for 2 days at 60 °C.

Anal. Calcd for $PtCl_2(Ph_2PCH_2CCF_3CHPPh_2)$: C, 45.18; H, 3.11; P, 8.32. Found: C, 45.38; H, 3.07; P, 7.72. Ir (mull, cm^{-1}): ν(C–F) 1250 (vs), 1231 (w), 1192 (s), 1180 (s), 1165 (m), 1128 (vs),

1104 (vs); ν(Pt–Cl) 321 (s), 303 (s). NMR (100 MHz, CD$_2$Cl$_2$): δ 7.3–8.0 m (phenyl H), 6.85 (1:4:1 triplet of doublets) (vinyl H; J_{P-H} = 8 Hz, J_{Pt-CH} = 54 Hz), 3.24 (1:4:1 triplet of doublets) (CH$_2$; J_{P-H} = 12 Hz, J_{Pt-CH_2} = 70 Hz).

cis-$Pt(CNS)_2(Ph_2PCH_2CCF_3CHPPh_2)$. This complex was prepared from the chloride by metathesis with KSCN in warm acetonitrile. Recrystallization from dichloromethane–ethanol afforded pale yellow crystals.

Anal. Calcd for $Pt(CNS)_2(Ph_2PCH_2CCF_3CHPPh_2)$: C, 45.62; H, 2.94; N, 3.55. Found: C, 45.62; H, 3.15; N, 3.44. Ir (mull, cm^{-1}): ν(C$\equiv$N) 2130 (s, sp), 2104 (s, br); ν(C–F) 1250 (vs), 1216 (w), 1180 (vs), 1160 (w), 1140 (s), 1132 (s), 1100 (s). NMR (60 MHz, CD$_2$Cl$_2$): δ 7.35–8.05 m (phenyl H), 6.90 m (vinyl H), 3.32 (1:4:1 triplet of double doublets; CH$_2$; $^{2or4}J_{P-H}$ = 20 Hz, $^{4or2}J_{P-H}$ = 11 Hz, J_{Pt-CH_2} = 107 Hz). The ^{15}N-substituted complexes $M(CNS)_2$-$(Ph_2PCH_2CCF_3CHPPh_2)$ (M = Pd, Pt) were prepared on the 100-mg scale by metathesis of the chlorides with NaSC^{15}N (90% enriched) in warm acetonitrile. The purity of the products was checked by infrared spectroscopy. For M = Pd, ν(C$\equiv^{15}$N) bands appear at 2098 (s, sp), 2090 (s, sp) cm^{-1} (cf. ν(C$\equiv$N) 2121 (s, sp), 2113 (s, sp) cm^{-1}),[9] and for M = Pt, ν(C$\equiv^{15}$N) bands are at 2104 (s, sp), 2078 (s, br) cm^{-1}.

Physical Measurements. Infrared spectra were measured on a Perkin-Elmer 180 spectrophotometer using Nujol mulls on CsI plates for solids and as solutions in 0.5-mm matched sodium chloride cells. ^{31}P NMR measurements were made using Jeol PFT-100L and Bruker HFX-90 Fourier transform spectrometers operating at 40.48 and 36.43 MHz, respectively. For the former instrument CH$_2$Cl$_2$ solutions were used with the D lock provided by a deuteriobenzene solution of the external standard P(OMe)$_3$. For the latter instrument CD$_2$Cl$_2$ solutions were used the D lock being provided by solvent. External, 85% H$_3$PO$_4$ was used as a reference. All spectra were broad band proton decoupled. Shifts are reported in ppm upfield from trimethyl phosphite which has a shift of –141 ppm from 85% H$_3$PO$_4$. Coupling constants are in Hz.

Results and Discussion

The synthesis of the unsymmetrical diphosphine complexes cis-$PdX_2(Ph_2PCH_2CCF_3CHPPh_2)$ (X = Cl, Br, CNS) via base-promoted coupling of two cis coordinated phosphinoacetylenes has been previously described in detail.[9] The corresponding platinum compounds cis-PtX_2-$(Ph_2PCH_2CCF_3CHPPh_2)$ (X = Cl, CNS) are most conveniently prepared via the reaction of K$_2$PtCl$_4$ or K$_2$Pt(SCN)$_4$ with 2 mol of the ligand $Ph_2PC\equiv CCF_3$ in the presence of water although prolonged hydrolysis of cis-$PtCl_2(Ph_2PC\equiv CCF_3)_2$ also affords the chloride complex in good yield. The appearance of two ν(Pt–Cl) bands at 321, 303 cm^{-1} in the far-infrared spectrum of $PtCl_2(Ph_2PCH_2CCF_3CHPPh_2)$ unequivocally establishes a cis stereochemistry in the solid state. In the ν(C$\equiv$N) region the complex $Pt(CNS)_2$-$(Ph_2PCH_2CCF_3CHPPh_2)$ has two bands, one sharp (2130 cm^{-1}) characteristic of S-bonded CNS$^-$ and the other broad (2104 cm^{-1}) indicative of N-bonded thiocyanate. These bands

Table I. Phosphorus NMR Data for cis-MX$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$)^a

Complex	Probe temp, °C	$\delta_P{}^b$	$\delta_{P'}$	$J_{P-P'}$	J_{M-P}	$J_{M-P'}$	$J_{^{15}N-P}$ (trans)	$J_{^{15}N-P'}$ (trans)
PdCl$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$)	-60	+72.39	+129.13					
PtCl$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$)	30	+106.36	+147.85	19.53	3703	3459		
Pd(SC^{15}N)$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$)	-69	+71.79	+130.12	14.65				
Pd(SC^{15}N)(^{15}NCS)(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$)^c	-60	+70.10	+126.14	14.65				53.71
Pd(^{15}NCS)(SC^{15}N)(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$)^d	-60	+87.07	+136.4	19.54			53.71	
Pt(SC^{15}N)$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$)	30	+97.32	+143.14	24.41	3259.3	2984.6		
Pt(SC^{15}N)(^{15}NCS)(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$)^c	30	+101.09	+150.26	26.86	3172.6	3334.9		56.15
Pt(^{15}NCS)(SC^{15}N)(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$)^d	30	+117.03	+148.18	26.86	3520.5	2895.5	57.37	
Pt(^{15}NCS)$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$)	30	e	+153.7	26.85		3335^f		57.3

^{a} Chemical shifts in ppm upfield from (MeO)$_3$P; coupling constants in Hz. ^{b} P is the phosphorus atom attached to -CH= (see text). ^{c} ^{15}NCS trans to P'. ^{d} ^{15}NCS trans to P. ^{e} Hidden under other P resonances. ^{f} Estimate only; satellites poorly defined.

persist in solution (CHCl$_3$, ν(C≡N) 2112 (s, sp), 2097 (s, br) cm^{-1}; CH$_3$COCH$_3$, ν(C≡N) 2112 (sh), 2097 (s, br) cm^{-1}) indicating either that a mixed species Pt(NCS)(SCN)-(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) is present or that there is a mixture of dithiocyanato and diisothiocyanato isomers. In the ^{1}H NMR spectrum of PtCl$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) both the vinyl and methylene resonances are 1:4:1 triplets of double doublets due to the presence of both ^{31}P-H and ^{195}Pt-H coupling. The corresponding thiocyanate has a methylene resonance consisting of a 1:4:1 triplet of double doublets. Hence both phosphorus nuclei are coupled to the -CH$_2$- protons as in the palladium complexes.[9] Unfortunately, since it is not known with certainty whether the two-bond or four-bond P-H coupling is larger, these assignments cannot be distinguished.[11] The proton-decoupled ^{31}P NMR spectra of MCl$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) (M = Pd, Pt) (Table I) are unambiguous. For M = Pd two single chemically shifted resonances due to the nonequivalent phosphorus atoms are observed. The chemical shift difference of 57.74 ppm is appreciable and compares with a difference of 95.6 ppm between the phosphine and phosphinite resonances in cis-PdCl$_2$(Ph$_2$PCH$_2$CH$_2$OPPh$_2$).[14] It is interesting that $J_{P-P} \sim$ 0 for this complex. The spectrum of the platinum analogue consists of two doublets (J_{P-P} = 19.53 Hz) with a chemical shift difference of 41.48 ppm, together with platinum-195 satellites. The values of $^1J_{^{195}Pt-P}$ (3703 and 3459 Hz) are typical for phosphines trans to chloro ligands.[15] The larger ^{195}Pt-^{31}P coupling constant is associated with the phosphorus nucleus at lowest field. Since J_{Pt-P} values are known to be sensitive to the electronegativity of phosphorus substituents, with the more electronegative groups giving rise to the larger couplings,[16] the low-field resonance can be confidently assigned to the phosphorus atom bonded to the vinyl group. This conclusion gains support from the x-ray data for Pd-(SCN)$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$)[17] where the Pd-P(CH) bond length is apparently shorter than the Pd-P(CH$_2$) length. Metal-phosphorus bond lengths correlate well with M-^{31}P coupling constant magnitudes.[18]

For a cis square-planar metal(II) thiocyanate complex containing an unsymmetrical di(tertiary phosphine) ligand four isomeric species (A-D) are possible in solution (neglecting ionic and thiocyanate-bridged species). The two mixed species C and D differ from one another on account of ligand asymmetry. If all four species were present simultaneously, the ^{31}P spectrum of a solution would exhibit eight doublets provided J_{P-P} > 0 and the coupled nuclei gave AX type spectra.

The ^{31}P NMR spectrum of Pd(CNS)$_2$-(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) at ambient temperature consists of two very broad resonances (full width at half-height ca. 200 Hz) separated by a chemical shift difference of 54.37 ppm. This broadening of the resonances of the two inequivalent phosphorus nuclei must be due to an exchange phenomenon
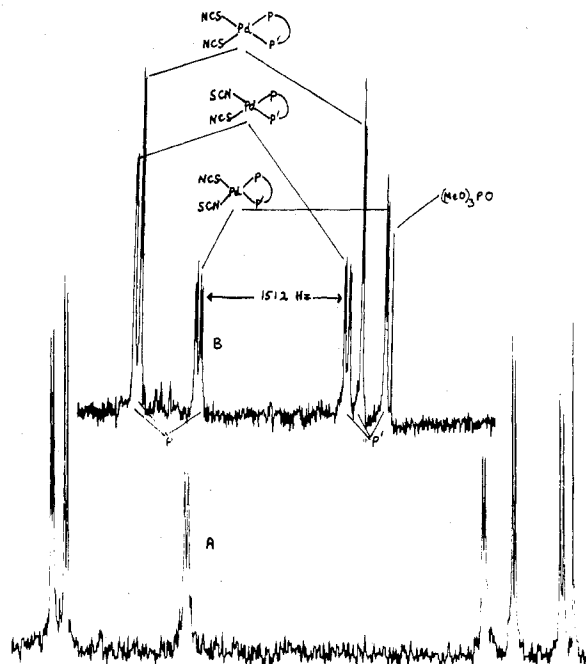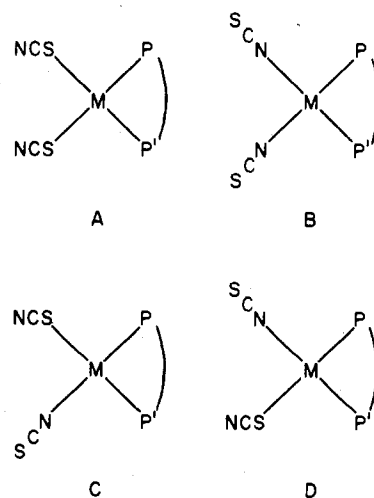

Figure 1. ^{31}P NMR spectra: A, Pd(CNS)$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) in CH$_2$Cl$_2$ at -69 °C; B, Pd(C^{15}NS)$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) in the same solvent at -60 °C. An assignment of resonances to the various species is given. P and P' refer to phosphorus atoms attached to -CH= and -CH$_2$- groups, respectively.

A   B

C   D

involving the thiocyanate groups since it is not apparent in the chloride complex. On cooling to -60 °C a dramatic change occurs giving a spectrum with six doublets grouped in two sets of three (Figure 1). The chemical shift difference between
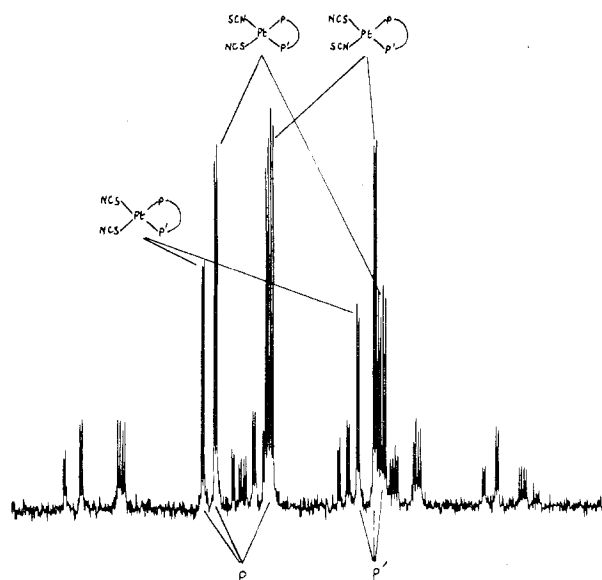
Figure 2. ^{31}P NMR spectrum of Pt(C^{15}NS)$_2$(Ph$_2$PCH$_2$CCF$_3$CH-PPh$_2$) in CH$_2$Cl$_2$ at +30 °C.

the two sets suggests, by analogy with the spectrum of the chloride complex, that the low-field resonances are due to phosphorus nuclei of Ph$_2$PCH= groups. The presence of only six doublets indicates that one of the species A–D is missing. The identity of the solution species is unambiguously revealed by the ^{31}P spectrum of the isotopically substituted complex Pd(C^{15}NS)$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) (Figure 1). While four doublets remain unchanged, two resonances appear as quartets due to additional coupling of phosphorus nuclei to ^{15}N(I = 1/2) nuclei of trans N-bonded thiocyanates. Moreover, the values of $^2J_{P-P'}$ (Table I) uniquely establish that the low-field quartet resonance ($J_{P-P'}$ = 19.54 Hz) arises from a phosphorus atom in the same ligand and hence indicates the same chemical species as the high-field doublet. This species is thus the mixed thiocyanate complex C where the Ph$_2$PCH= group is trans to the isothiocyanate. Similarly, the high-field quartet and lowest field doublet are due to species D. The absence of ^{15}N–^{31}P coupling or line broadening in the two remaining doublets implies that these resonances arise from the dithiocyanato species A. The occurrence of ^{15}N–^{31}P coupling between trans N-bonded thiocyanates and phosphines parallels our observations on the phosphite complexes cis-Pt(NCS)-(SCN)[P(OPh)$_3$]$_2$ although, for the latter, the additional presence of a diisothiocyanato species was discerned from the appearance of a deceptively simple AA'XX' (A = ^{31}P, X = ^{15}N) resonance.[7] The values of $J_{^{15}N-P}$ (Table I) are the first measured for Pd(II). Their magnitudes (53.71 Hz) are somewhat smaller than in cis-Pt(NCS)(SCN)[P(OPh)$_3$]$_2$ (91 Hz) and probably reflect the poorer trans influence of a phosphite than a phosphine[7,15] as well as the change of metal atom.

The spectra of the platinum complexes Pt(CNS)$_2$-(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) and Pt(C^{15}NS)$_2$-(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) (Figure 2) illustrate the wealth of coupling constant data available in favorable circumstances from complexes of a metal with I = 1/2. The assignment follows directly from that of the palladium analogue and the phosphite species cis-Pt(CNS)$_2$[P(OPh)$_3$]$_2$.[7] Again ^{15}N–^{31}P coupling is apparent in the mixed isotopically substituted species. However, no cis ^{15}N–^{31}P coupling, such as might be expected from a mixed complex (C or D), is measurable. In contrast with Pd(CNS)$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$), ^{14}N–^{31}P coupling is apparent in the resonances of phosphorus nuclei trans to isothiocyanates in the mixed species Pt(NCS)-(SCN)(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$). These multiplets are not

simple 1:1:1 triplets of doublets as for cis-Pt[P(OPh)$_3$]$_2$-(NCS)(SCN)[7] and were not analyzed further. Values of $^2J_{P-P'}$ (Table I) are larger for the platinum complexes than the palladium species and can be compared with values of –8.0 Hz in cis-PdCl$_2$(PMe$_3$)$_2$, –18.9 Hz in cis-PtCl$_2$(PMe$_3$)$_2$,[19] and 9 Hz in PdCl$_2$[(dpp)$_2$op].[14] It is clear from recent work that $^2J_{PP}$ for cis palladium–phosphine complexes is generally small (usually <20 Hz) while the trans isomers have much larger coupling constants.[19,20] The ^{195}Pt–^{31}P coupling constants, measured from satellite resonances, serve to confirm the structural assignment, with $^1J_{^{195}Pt-P}$ always larger when the phosphorus atom in question is trans to the poorer trans-directing ligand, viz., isothiocyanate.[2,3] The much smaller values of $J_{^{195}Pt-P}$ here than in cis-Pt(NCS)(SCN)[P(OPh)$_3$]$_2$ are notable.

There are some interesting chemical shift changes for the two phosphorus nuclei as the trans ligand is changed from sulfur (in M(SCN)$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$)) to nitrogen. For the low-field resonance (P—CH=) a large upfield shift (M = Pd, +15.26 ppm; M = Pt, +19.71 ppm) occurs while for the high-field resonance (P—CH$_2$) a low-field shift occurs for Pd (–3.98 ppm) and a high-field shift (+7.12 ppm) for platinum. These changes, for which an explanation is not readily apparent, emphasize the dangers of using chemical shift correlations for structural assignments, especially for mixed anion complexes.

In both the palladium and platinum systems investigated the species concentrations, as measured from relative peak heights,[21] were found to be in the order M(NCS)(SCN) ≫ M(SCN)$_2$ ⋙ M(NCS)$_2$. Indeed the diisothiocyanate complex was not observed at all in the ^{31}P spectra of the palladium thiocyanate complex. A very weak quartet resonance at δ +153.7 ppm may be evidence for the diisothiocyanate Pt(^{15}NCS)$_2$(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) in the spectrum of the platinum analogue. It is of interest that a recent study by ^{1}H{^{195}Pt} INDOR spectra[22] of thiocyanate bonding in Pt(CNS)$_2$(SMe$_2$)$_2$ also revealed a preponderance of S-bonded species over N-bonded thiocyanates. These results are of significance since they indicate that the stabilization of M–SCN (M = Pd, Pt) bonding in crystalline phosphine (or sulfide) complexes may not be simply an artifact of solubility or solid-state effects. In the solid state Pd(SCN)$_2$-(Ph$_2$PCH$_2$CCF$_3$CHPPh$_2$) is completely S bonded[17] while the platinum analogue has both S- and N-bonded thiocyanates. Thus the solid-state and solution studies of these complexes parallel the results for M(CNS)$_2$(Ph$_2$PC≡C-t-Bu)$_2$[3] where the platinum atom exhibits a more pronounced tendency than palladium to bind to the isothiocyanate group. A detailed ^{31}P NMR study of the behavior of metal(II) thiocyanate complexes with phosphines varying widely in steric and electronic properties is under way in an attempt to rationalize thiocyanate bonding patterns in solution.

cis-PtCl$_2$(Ph$_2$PC≡CCF$_3$)$_2$, 53426-08-7; ^{31}P, 7723-14-0.

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Carbon-13 Nuclear Magnetic Resonance Studies of Platinum(II)–Olefin Bonds

DAVID G. COOPER and JOHN POWELL*

^{13}C NMR data are reported for the series of platinum(II) compounds *trans*-[(olefin)PtCl$_2$(NC$_5$H$_4$Me)], K[(olefin)PtCl$_3$], and [(olefin)PtCl(NH$_3$)$_2$]BF$_4$ (where olefin may be *p*-YC$_6$H$_4$CH═CH$_2$, RCH═CH$_2$, RHC═CHR, or CH$_2$═CH(CH$_2$)$_n$X). The observed trends in $^1J^{195}$Pt–^{13}C and δ_C values of the olefinic carbon atoms are discussed in terms of the nature of olefin–platinum(II) bonding. The data can be rationalized qualitatively using a valence-bond description of the bonding. In terms of the Chatt–Dewar model of the bonding, the data support the view that donation from olefin π to a platinum σ orbital is the predominant component of the olefin–metal bond. The data also illustrate the varied effects of olefin substituents on the nature of platinum(II)–olefin bonds.

Introduction

Recent years have seen a rapid growth in the application of ^{13}C NMR to bonding and structural studies in organometallic chemistry. While ^{13}C NMR investigations of π-bonded olefin–transition metal complexes are now commonplace,$^{1-21}$ there is still considerable uncertainty and controversy concerning the unusual magnitudes of the ^{13}C coordination chemical shifts of olefins and the possible relationship with π-back-bonding effects.$^{2,3,5,16,17,20-22}$ Recent studies of organoplatinum compounds clearly emphasize the importance of systematic studies of closely related series of compounds and the added advantages of studying systems where both olefinic carbon shieldings and metal–olefinic carbon coupling constant data are available.$^{2-6}$

In this paper we report a systematic ^{13}C NMR spectroscopic study of both functionally substituted olefins and simple alkenes coordinated to platinum(II) in the three series of complexes **1–3**. These series provide examples of olefin

coordination to neutral, anionic, and cationic platinum(II).

In view of the extensive studies by Orchin and others of complexes of type **1** and thus the available literature data$^{23-31}$ the major portion of our studies has been confined to series **1** compounds with anionic **2** and cationic **3** analogues being studied for particularly interesting cases.

Very few of the previously reported ^{13}C NMR studies have concentrated on the effects of functional substitution of the olefin on coordination chemical shifts and metal–carbon coupling constants.^{4,5,21}

Experimental Section

Complexes of the type *trans*-[(olefin)PtCl$_2$(NC$_5$H$_4$Me)] were prepared using the method of Orchin et al.^{23} The anionic complexes K[(olefin)PtCl$_3$] were prepared via the method of Saika et al.^{32} The cationic derivatives *trans*-[(olefin)PtCl(NH$_3$)$_2$]BF$_4$ were prepared according to the method of Gel'fman and co-workers^{33} with the exception that we have used AgBF$_4$ in place of AgNO$_3$ and used acetone as the solvent in lieu of water. Acetone–dichloromethane was found to be an excellent solvent for the recrystallization of these compounds.

The ^{13}C NMR spectra were measured on either a Varian XL-100-15 or a Varian CFT-20 spectrometer operating in the Fourier transform mode at 25.2 and 20.0 MHz, respectively. All spectra were determined with noise-modulated proton decoupling. Proton-coupled spectra were recorded where necessary for assignment purposes. In order to obtain accurate $^1J_{\text{PtC}}$ values it was frequently necessary to recrystallize the type **1** complexes several times in order to ensure that the samples contained no excess picoline.^{28,29} The observation of well-resolved ^{195}Pt satellite resonances for the β carbon of the coordinated picoline indicated that picoline exchange was slow on the NMR time scale. In most cases the effect of repeated recrystallizations was an increase in $^1J^{195}$Pt–olefinic ^{13}C values of ca. 1 Hz.

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