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The ^{13}C Nmr Spectrum of $Pt(PPh_3)_2(\eta^2\text{-}CS_2)$ – a Non-fluxional π-CS_2 Complex

P. J. VERGAMINI and P. G. ELLER

Los Alamos Scientific Laboratory, University of California, Los Alamos, N.M. 87545, U.S.A.

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The reactions of small molecule ligands bound to coordinatively unsaturated transition metal complexes have been of interest from the standpoint of bonding arguments as well as reactivity of coordinated ligands. Although carbon disulfide and carbon monosulfide complexes have been known and studied for some time, and have been shown to be surprisingly diverse in coordinating to transition metals, the structures of only a few such complexes are known [1–9]. One such compound of formally Pt(0) can be prepared by the known reaction:

$$Pt(PPh_3)_4 + CS_2 \rightarrow Pt(PPh_3)_2(\eta^2\text{-}CS_2) \qquad (1)$$

The product and its palladium analogue are known by X-ray diffraction to contain a distinctly non-linear carbon disulfide π-bonded to Pt through carbon and one sulfur [10, 11]. The PtP_2CS coordination unit deviates only slightly from planarity. We were interested in investigating the solution structure of this molecule by carbon-13 nmr spectroscopy, a powerful tool for determining solution stereochemistry of transition metal complexes [12]. We have, therefore, prepared the complex containing 95% enriched $^{13}CS_2$ and have observed the ^{13}C nmr spectrum in $CHCl_3$ solution at 19 °C.

The ^{13}C nmr spectrum of $Pt(PPh_3)_2(\eta^2\text{-}CS_2)$ in the CS_2 region is shown in Fig. 1. An AXX′ pattern due to coupling of the CS_2 carbon to both *cis* and *trans* phosphorus ligands was observed, demonstrating a rigid configuration consistent with the solid state structure. The carbon-13 nucleus is strongly coupled to one phosphorus but weakly coupled to the other phosphorus. It is likely that the stronger coupling is due to the *trans* phosphorus, as was observed [9] with the square planar molecule *cis*-$[PtMe_2(PMe_2Ph)_2]$ [12, 13]. This trend in $^2J(^{31}P\text{–}M\text{–}^{13}C)$ couplings (*trans* > *cis*) also holds for octahedral mixed carbonyl-phosphine compounds of Mo and W [12]. We also observed coupling to ^{195}Pt (33.8% natural abundance, spin 1/2) in $Pt(PPh_3)_2(\eta^2\text{-}CS_2)$.

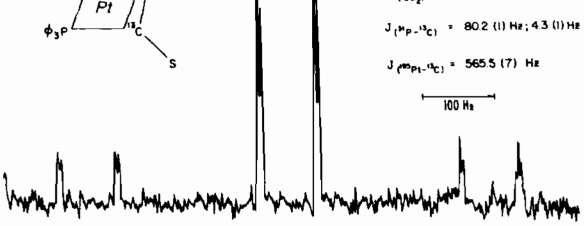

Fig. 1. Carbon-13 nmr spectrum of the bound CS_2 in $Pt(Ph_3)_2(\eta^2\text{-}CS_2)$ at 19 °C.

The observed spin–spin couplings demonstrate the absence of rotation of the π-CS_2 group about the metal–CS_2 bond, as well as other types of fluxional behavior, on the nmr time scale. These couplings do not collapse in the presence of either excess phosphine or excess CS_2, indicating that rapid exchange of ligands is not occurring. The ^{13}C absorption in the phenyl region was not unusual for this type of complex [12].

In contrast to $(PPh_3)_2Pt(\eta^2\text{-}CS_2)$ the complex $CpMn(CO)_2(\pi\text{-}CS_2)$ gives a temperature dependent ^{13}C-nmr spectrum indicative of fluxional behavior above 200 K [4, 5]. Below this temperature rotation of the CS_2 ligand about the axis of the coordinative bond becomes slower, as demonstrated by the reversible splitting of a single carbonyl resonance into two separate resonances.

Experimental

$Pt(PPh_3)_2(\eta^2\text{-}CS_2)$, containing 95% enriched $^{13}CS_2$ [14], was prepared by the reported procedure [15]. The nmr spectrum was obtained using a Varian XL-100 spectrometer in the Fourier Transform mode as described previously [16]. The spectrum was analyzed by a least-squares line-shape analysis code which fits the digitized spectrum to a set of Lorentzian lines. The spectrum was obtained from 4240 transients of 2048 data points and a spectrum width of 800 Hz. The chemical shift and coupling data are: $\delta = -59.9(1)$ ppm relative to CS_2 in $CHCl_3$ ($\delta = -253.2$ ppm relative to external TMS); $^2J(^{13}C\text{–}^{31}P) = 80.3(1)$ Hz, 4.3(1) Hz; $J(^{13}C\text{–}^{195}Pt) = 565.5(7)$ Hz.

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