^{14}N–^{31}P, ^{15}N–^{31}P, and ^{31}P–^{31}P Coupling Constants From the ^{31}P Nuclear Magnetic Resonance Spectra of Square Planar Platinum(II) and Palladium(II) Thiocyanate Complexes

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Summary The ^{31}P n.m.r. spectra of *cis*-$PtX_2[P(OPh)_3]_2$ (X = CNS, $C^{15}NS$) show the independent existence of dithiocyanato, diisothiocyanato and mixed linkage isomers in solution, and the appearance of distinct resolvable ^{31}P–^{31}P, ^{14}N–^{31}P and ^{15}N–^{31}P coupling in the spectra of the mixed species suggests a means of measuring these couplings in co-ordination complexes.

Considerable effort has been devoted to the measurement and interpretation of ^{31}P–^{31}P coupling constants in phosphine complexes.[1] Recent developments have included the synthesis by Grim and his co-workers of unsymmetrical ditertiary phosphine complexes as a means of obtaining J_{P-P} from direct measurements in ^{31}P spectra[2] and the application of elegant double resonance, spin tickling and computer simulation techniques to the indirect determination of J_{P-P}.[3] During the course of studies designed to identify thiocyanate linkage isomers in solution we found that the ^{31}P n.m.r. spectra of *cis*-$M(CNS)_2L_2$† [M = Pt; L = Ph_2PC_2R, $P(OR)_3$] are a rich source of ^{31}P–^{31}P coupling constants owing to the preponderance of mixed (SCN)(NCS) species in solution. Moreover ^{14}N–^{31}P coupling is also clearly resolved in these spectra and we now report the first values for $J_{^{14}N-^{31}P}$ in co-ordination complexes together with the corresponding ^{15}N coupling constants from ^{15}N isotopically substituted complexes. The use of CNS^- ligands (as opposed to halides) may provide a direct method of obtaining J_{P-P} for phosphine complexes without recourse to more elaborate indirect methods,

The ^{31}P Fourier transform n.m.r. spectra of *cis*-Pt(NCS)(SCN) $[P(OPh)_3]_2$ or *cis*-$Pt(NCS)_2[P(OPh)_3]_2$‡ and the corresponding ^{15}NCS isotopically substituted compounds are shown in the Figure. The spectra consist of four central resonances with attendant satellites due to coupling with $^{195}Pt(I = \frac{1}{2}$, 33%). Chemical shifts and coupling constants are given in the Table. The spectra are consistent with the co-existence of *cis*-$Pt(SCN)_2[P(OPh)_3]_2$ (**1**) (resonance A), *cis*-Pt(NCS)(SCN)$[P(OPh)_3]_2$ (**2**) (resonances B and B′) and *cis*-$Pt(NCS)_2$ $[P(OPh)_3]_2$ (**3**) (resonance C) in solution, with the mixed species predominating.§ Species (**1**) has two chemically equivalent phosphorus atoms and gives a singlet ^{31}P resonance. An AB (or AX) spectrum might be expected from the two inequivalent phosphorus atoms in (**2**). Additional $^{14}N(I = 1)$ coupling to ^{14}N nuclei of the isothiocyanate group *trans* to phosphorus gives a triplet of doublets for one ^{31}P resonance which appears as a doublet of doublets in the spectrum of the ^{15}N-substituted species. Additionally, a small *cis*-coupling is resolved in the ^{31}P resonance of the phosphorus *trans* to the thiocyanate group consistent with the higher resonance frequency of ^{15}N compared to ^{14}N at a given field strength. The couplings ^{195}Pt–P are readily extracted from satellite resonances,

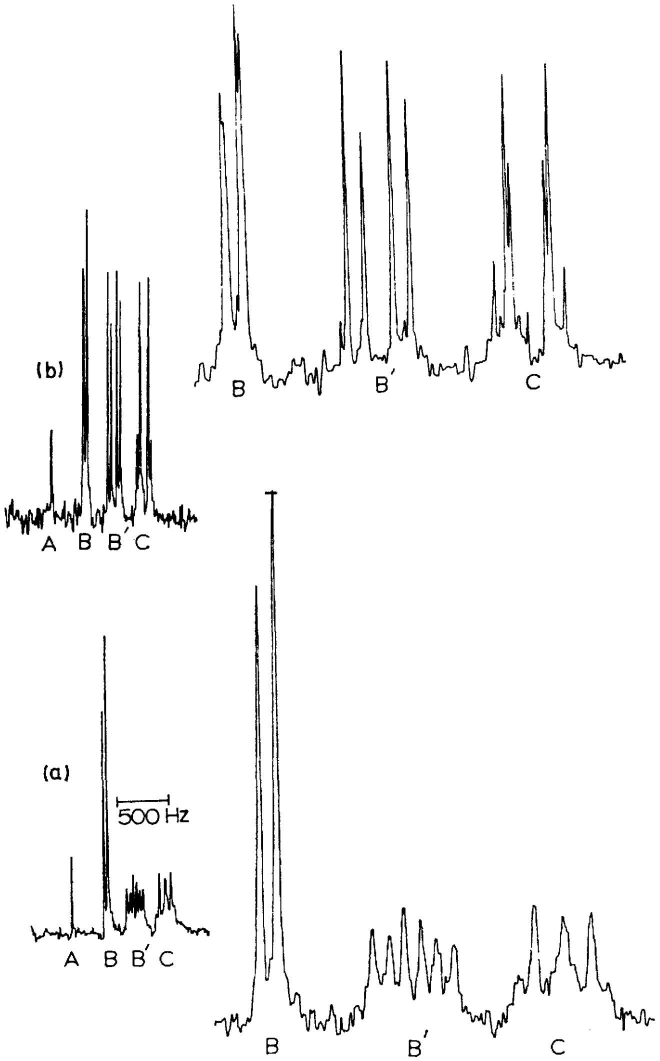

Figure. The central portion (^{195}Pt satellites not shown) of the ^{31}P spectra of (a) *cis*-$Pt(CNS)_2[P(OPh)_3]_2$ and (b) *cis*-$Pt(C^{15}NS)_2$ $P(OPh)_3]_2$ in CH_2Cl_2 at 30°C.

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† The thiocyanate ion is written as CNS when no particular bonding mode is implied.

‡ The spectra appear to be independent of the isomer dissolved.

§ This result represents the first unequivocal identification of mixed species Pt(NCS)(SCN)L_2 as opposed to mixtures of $Pt(NCS)_2L_2$ and $Pt(SCN)_2L_2$ in solution. *cis*-Pt(NCS)(SCN)$[P(OPh)_3]_2$ has been isolated in the solid state.[4]

TABLE

Chemical shifts[a]/p.p.m. and coupling constants/Hz for *cis*-$\mathrm{Pt(CNS)_2[P(OPh)_3]_2}$ in solution

Species		δ	$^2J^{cis}_{\mathrm{P-P}}$	$^2J^{cis}_{\mathrm{P-N}}$	$^2J^{trans}_{\mathrm{P-N}}$	$^1J_{\mathrm{Pt-P}}$	$^2J^{cis}_{\mathrm{N-N}}$
cis-$\mathrm{Pt(SCN)_2[P(OPh)_3]_2}$		+68·7				5188	
cis-$\mathrm{Pt(NCS)(SCN)[P(OPh)_3]_2}$	P *trans* to S	+77·2	34	<3		4946	
	P *trans* to N	+84·2	34		63	5670	
cis-$\mathrm{Pt(NCS)_2[P(OPh)_3]_2}$		+91·7				5636	
cis-$\mathrm{Pt(SC^{15}N)_2[P(OPh)_3]_2}$		+68·8				5190	
cis-$\mathrm{Pt(^{15}NCS)(SC^{15}N)[P(OPh)_3]_2}$	P *trans* to S	+77·1	34	6		4950	
	P *trans* to N	+84·2	34		91	5672	
cis-$\mathrm{Pt(^{15}NCS)_2[P(OPh)_3]_2}$		+91·6	36[b]	7[b]	95[b]	5644	2[b]

[a] Measured in $\mathrm{CH_2Cl_2}$ at 30° from external trimethylphosphite standard. Trimethylphosphite has δ −28·5 p.p.m. from $\mathrm{P_4O_6}$.[1]
[b] Approximate estimate only.

these (Table) being typical of *cis*-platinum(II) complexes.[1] The resolution of ^{14}N–P coupling is unprecedented and presumably reflects a slow relaxation of ^{14}N nuclei and a small electric field gradient at the nucleus. It is of interest that unresolved ^{14}N–H or ^{14}N–P coupling has been postulated as an explanation of line broadening in the ^{1}H n.m.r. spectrum of *trans*-$\mathrm{PtH(NCS)(Et_3P)_2}$[5] and in the ^{31}P spectrum of *trans*-$\mathrm{PtX\{(PhO)_2PO\}(Bu_3P)_2}$($\mathrm{X = NCO, NCS}$).[6] The *N*-bonded species (**3**) gives a deceptively simple AA′XX′ ($\mathrm{X} = {}^{14}\mathrm{N}$; $I = 1$) spectrum which is simplified on ^{15}N substitution. The separation of the intense lines in the ^{15}N substituted species ($J_{\mathrm{AX}} + J_{\mathrm{AX}'}$) is 88 Hz; other parameters derived from the analysis are given in the Table. The couplings J_{AX} and $J_{\mathrm{AX}'}$ appear to be opposite in sign. A complete analysis of both spectra is in progress.

We have observed similar spectra for phosphinoacetylene complexes *cis*-$\mathrm{Pt(CNS)_2(Ph_2PC{\equiv}CR)_2}$($\mathrm{R{=}Bu^t}$, Et, Ph) where ^{31}P–^{31}P, ^{14}N–^{31}P and ^{15}N–^{31}P coupling constants are readily obtained from the ^{31}P resonances of the mixed species. Corresponding palladium complexes are labile in solution and only exchange-broadened single-line spectra are observed at 30°. At −60° the spectra of all three species can be seen with the ratios being *cis*-$\mathrm{Pd(NCS)(SCN)L_2}$ > *cis*-$\mathrm{Pd(SCN)_2L_2}$ > *cis*-$\mathrm{Pd(NCS)_2L_2}$ [$\mathrm{L = Ph_2PC{\equiv}CR, P(OPh)_3}$]. However ^{14}N–^{31}P coupling is unobserved and $^2J^{cis}_{\mathrm{P-P}}$ is small ($\leqslant$ 10 Hz) or unresolved.

We thank Dr. A. Pidcock and Dr. T. E. Gough for valuable discussion, the School of Molecular Sciences, University of Sussex for the ^{31}P spectra and M. Siverns for running the spectra.

(*Received*, 3*rd December* 1974; *Com.* 1466.)

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