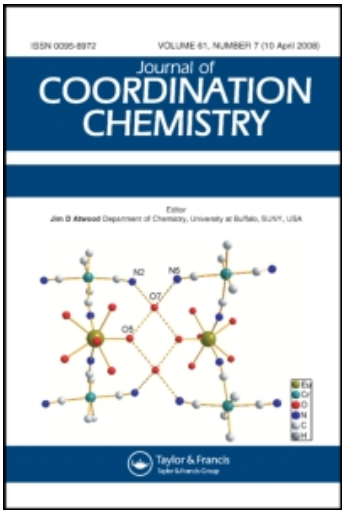

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^{15}N AND ^{31}P NMR STUDIES OF CYANO(TRIALKYL/TRIARYL)PHOSPHINE GOLD(I) COMPLEXES

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^{15}N AND ^{31}P NMR STUDIES OF CYANO(TRIALKYL/TRIARYL)PHOSPHINE GOLD(I) COMPLEXES

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The ligand scrambling reaction of $R_3PAuC^{15}N$ to form $(R_3P)_2Au^+$ and $Au(C^{15}N)_2^-$ has been studied (by ^{15}N and ^{31}P NMR spectroscopy) for R = Me, Et, *i*-Pr, and Ph. ^{31}P NMR showed two resonances due to R_3PAuCN and $(R_3P)_2Au^+$ species, while ^{15}N NMR showed only an averaged resonance due to $R_3PAuC^{15}N$ and $Au(C^{15}N)_2^-$ species, except for $Et_3PAuC^{15}N$, for which two separate resonances were detected. $R_3PAu^{13}C^{15}N$ (where R = Me, Et and Ph) complexes were also prepared and $^2J(^{31}P\text{-}^{13}C)$ as well as $^3J(^{31}P\text{-}^{15}N)$ constants were measured. The free activation energy for ligand scrambling in Ph_3PAuCN was determined by ^{31}P NMR band shape analysis to be 39.7 kJ/mol^{-1}.

KEYWORDS: gold, phosphines, cyanide, nmr, scrambling

INTRODUCTION

Recent solid state studies[1–3] of cyano(trialkyl)phosphinegold(I) complexes have shown that they form linear gold(I) species. However, in solution, these complexes undergo a ligand scrambling reaction as shown in (*1*).[2,4]

$$2R_3PAuCN \rightleftharpoons (R_3P)_2Au^+ + Au(CN)_2^- \qquad (1)$$

The equilbrium constant for these reaction is dependent[4] upon extrinsic effects such as initial concentration of the complexes, $[R_3PAuCN]_0$, and ionic strength of the medium, and intrinsic factors such as the steric effects and electronic properties of the phosphine ligands. These ligand scrambling reactions are important from a biological point of view. Smokers who are treated with various anti-arthritic gold drugs were reported to have higher concentration of gold in their red blood cells as compared with nonsmokers.[5–7] Possible mechanisms by which the gold in the form of $Au(CN)_2^-$ can enter into red blood cells is the subject of several recent studies.[8–12] The very large formation constant for $Au(CN)_2^-$ (reported to be log β_2 36.6,[13]) drives all L-Au-CN complexes (where L = thiolate- or phosphine-containing

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ligands) to disproportionate as in (*1*) thus generating $Au(CN)_2^-$ which can enter into red blood cells. Thiolate-based drugs do not enter red blood cells because they are in a polymeric form.[11,14,15]

We have recently reported the disproportionation of gold(I)-thiomalate and gold(I)-thioglucose in the presence of $C^{15}N^-$ by using ^{15}N NMR spectroscopy.[16] At 1:<2 AuSR:$C^{15}N^-$ ratio, two resonances were observed for $Au(C^{15}N)_2^-$ and RS-Au-$C^{15}N^-$. At a 1:2 ratio of AuSR:$C^{15}N^-$, only one resonance was observed for $Au(C^{15}N)_2^-$ complexes, which means that all the thiolate ligands are released in solution. In the present study, we have synthesised ^{15}N labelled $R_3PAuC^{15}N$ complexes to see if the ligand scrambling reaction can be followed by ^{15}N NMR spectroscopy and also to compare ^{15}N chemical shifts of RS-Au-$C^{15}N^-$ with R_3P-Au-$C^{15}N$ complexes. We have also prepared doubly labelled R_3P-Au-$^{13}C^{15}N$ (where R = Me, Et and Ph) complexes, where all relevant coupling constants were measured.

EXPERIMENTAL

Reagents

$KC^{15}N$ (99%) and $K^{13}C^{15}N$ (99%) were purchased from Merck Sharp and Dohme, Canada. Sodium tetrachloroaurate dihydrate, phosphine ligands (trimethyl, triethyl, triphenyl, triisopropyl) were obtained from Strem Chemical Co. CD_3OD was obtained from Fluka Chemical Co.

R_3PAuCl

All the R_3PAuCl complexes were prepared by the addition of phosphine ligands to an ethanolic solution of $NaAuCl_4$ as described in the literature.[17–18]

$R_3PAuC^{15}N$

Tri(alkyl/aryl) phosphinegold(I) cyanide complexes were prepared by adding solid $KC^{15}N$ (10% labelled) directly to an alcoholic solution of R_3PAuCl. Elemental analysis, melting points and percentage yields for $R_3PAuC^{15}N$ (R = Me, Et, *i*-Pr, Ph) complexes are given in Table 1.

Table 1 Elemental analyses of $R_3PAuC^{15}N$ complex, melting points and % yield.

R	Found (calcd.)%			Found(lit.) m.pt.		% yield
	C	H	N			
Me	15.94 (16.0)	2.97 (3.0)	3.86 (5.0)	201		80
Et	25.08 (24.58)	4.54 (4.39)	4.16 (4.39)	109	(113)[a]	41
i-Pr	31.64 (31.27)	5.77 (5.47)	3.80 (3.91)	108		54
Ph	46.23 (46.93)	3.29 (3.08)	2.81 (3.08)	209	(204)[a]	90

[a]References 2 and 4.

$R_3PAu^{13}C^{15}N$

These complexes were synthesized as decribed above (R = Me, Et and Ph) using 99% label ^{13}C and 99% ^{15}N label $K^{13}C^{15}N$.

^{15}N and ^{31}P NMR Spectroscopy

^{15}N NMR spectra were obtained at 27.24 MHz on a Jeol 270 spectrometer using CD_3OD solutions at the probe temperature of 300 K. The chemical shifts for ^{15}N NMR spectra were measured using a sealed $NH_4{}^{15}NO_3$ solution as external reference, which has a resonance at 375.11 ppm relative to pure CH_3NO_2 380.2 ppm.[16,19]

We did not measure the T_1 values of any resonance. The spectrometer conditions were: 5.0 s delay time, 16 K data points, aquisition width 20,000 Hz, pulse width 6.0 μs (20°), and 10 mm multinuclear probe. For the ^{15}N NMR spectra, approximately 60,000 scans were accumulated for each sample.

^{31}P NMR spectra were obtained at 109.25 MHz using the above solutions at the probe temperature of 300 K. The ^{31}P NMR chemical shifts were measured against external 1% TMP.[20] T_1 values were previously reported[2,4] for these compounds and are in the range of 5–7 seconds. The spectrometer conditions were: 1.0 s delay time, 32 K data points, acquisition width 4,000 Hz, pulse width 5.0 μs, 10 mm multinuclear probe. For the ^{31}P NMR spectra, approximately 10,000 scans were accumulated. ^{15}N and ^{31}P NMR chemical shifts for various $R_3PAuC^{15}N$ complexes are given in Table 2, and ^2J and ^3J values are given in Table 3.

Calculations of Activation Parameters

The activation parameters were calculated from proton decoupled ^{31}P NMR spectra for Ph_3PAuCN (0.010 M in CD_3OD), recorded between +25°C and −60°C. At −60°C, two peaks due to Ph_3PAuCN and $(Ph_3P)_2Au^+$ are observed and these coalesce around −25°C. Above −20°C, the average peak becomes sharper. At temperatures below −30°C, integration of ^{31}P resonances gave relative concentrations of Ph_3PAuCN and $(Ph_3P)_2Au^+$ species and from this K_{eq} was calculated. K_{eq} was found to be constant at 0.14 for −60°C, −50°C and −40°C, within experimental error.

Band shape analysis was carried out on the basis of exchange between two non-coupled sites with unequal population, using a library package.[21] The life time and rate constant at different temperatures are given in Table 4. Activation energies

Table 2 ^{13}C, ^{15}N and ^{31}P NMR chemical shifts and K_{eq} data for $R_3PAuC^{15}N$ complexes.[a]

R	$\delta(^{15}N)$[b] R_3PAuCN	$\delta(^{13}C)$[d] R_3PAuCN	$\delta(^{31}P)$[c] R_3PAuCN	$\delta(^{31}P)$ $(R3P)_2Au^+$	(K_{eq})[d]	ν_{CO},cm^{-1}[e]
Me	263.0	158.3	−3.09	5.94	0.37	2064
Et	262.5	160.4	35.35	44.15	0.24	2062
i-Pr	262.2	160.9	66.10	75.20	0.29	2059
Ph	265.5	156.2	39.37	43.92	0.14	2069

[a]CD_3OD solvent. [b]In ppm relative to external $NH_4{}^{15}NO_3$. [c]In ppm relative to external 1% TMP. [d]Reference 4. [e]Reference 24.

Table 3 ^{31}P Coupling constant data for $R_3PAu^{13}C^{15}N$, where R = Me, Et, and Ph.

Compound	Temp. (K)	^2J (^{31}P-^{13}C) (Hz)	^3J (^{31}P-^{15}N) (Hz)
$Me_3PAu^{13}C^{15}N$	297	130.7(129.4)[a]	3.6
$Et_3PAu^{13}C^{15}N$	297	122.2(122.2)[a]	2.9
$Ph_3PAu^{13}C^{15}N$	213	124.6(126.0)[a]	4.0

[a]Reference 4.

Table 4 Life time[a] and rate constant data for the scrambling reaction of 0.010M Ph_3PAuCN in CD_3OD at K_{eq} = 0.14.

T/K	(τ_a/s)[a]	k/dm^3 mol^{-1}s^{-1}
233	0.0079	1840
243	0.0024	6056
253	0.00063	23,071
263	0.00030	48,450
273	0.00012	121,124

[a]Life time of the Ph_3PAuCN species.

were calculated from an Arrthenius plot of ln k_r *versus* 1/T and free energy of activation from an Eyring plot of ln (k_r/T) *versus* 1/T.

RESULTS AND DISCUSSION

^{31}P NMR spectra of 0.020 M Me_3PAuCN, Et_3PAuCN, *i*-Pr_3PAuCN and Ph_3PAuCN complexes in CD_3OD were measured. In each case two resonances assigned to R_3PAuCN and $(R_3P)_2Au^+$ were observed as indicated in (*1*) except for Ph_3PAuCN. Note that the ratios of R_3PAuCN and $(R_3P)_2Au^+$ resonances are different because K_{eq} is different for each complex,[4] as shown in Table 2.

Figure 1A, 1B and 1C shows the ^{15}N NMR spectra of $Me_3PAuC^{15}N$, $Et_3PAuC^{15}N$, and *i*-$Pr_3PAuC^{15}N$ complexes using the same sample as for the ^{31}P NMR measurements. The ^{15}N chemical shift difference between $Me_3PAuC^{15}N$ or *i*-$Pr_3PAuC^{15}N$ and $Au(C^{15}N)_2^-$ is very small and therefore only one set of resonances is observed. However, two resonances are observed for the $Et_3PAuC^{15}N$ complex. The less intense resonance at 264.0 ppm is due to $Au(C^{15}N)_2^-$ and the more intense resonance at 262.5 ppm is assigned to $Et_3PAuC^{15}N$.[4,6]

Figure 2 shows ^{31}P NMR spectra of $R_3PAu^{13}C^{15}N$ (R = Me, Et and Ph) complexes. Both $Me_3PAu^{13}C^{15}N$ and $Et_3PAu^{13}C^{15}N$ gave two sets of peaks due to $(R_3P)_2Au^+$ and $R_3PAu^{13}C^{15}N$ which split into two resonances due to $^2J(^{31}P$-$^{13}C)$ coupling.[2,4] The ^2J values are given in Table 3. However, $Ph_3PAu^{13}C^{15}N$ gave only one average resonance due to fast exchange between $(Ph_3P)_2Au^+$ and $Ph_3PAu^{13}C^{15}N$ species at room temperature, consistent with previous studies.[4] On cooling to $-60°C$, all species were in the slow exchange limit and resonances due to both $Ph_3PAu^{13}C^{15}N$ and $(Ph_3P)_2Au^+$ were observed as shown in Figure 2. ^3J splitting for $R_3PAu^{13}C^{15}N$ due to ^{31}P-^{15}N was also observed as shown in Figure 2 and reported in Table 3.

The X-ray structure of Me_3PAuCN, Et_3PAuCN, and Ph_3PAuCN shows that these complexes are linear in the solid state.[1–3] However, as soon as they are dissolved in solution,[2,4,22] these complexes undergo ligand scrambling reactions as shown in (*1*).

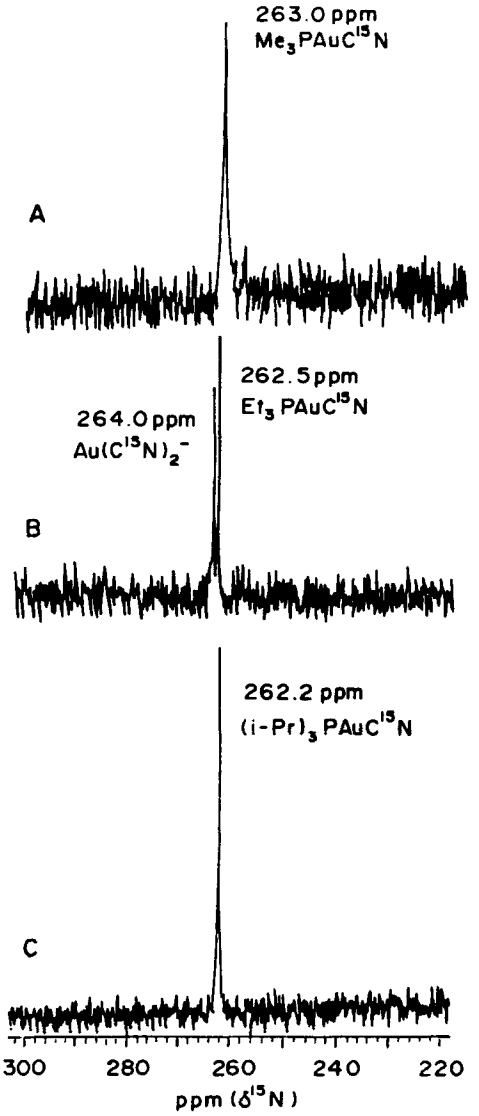

Figure 1 The 27.24 MHz ^1H noise-decoupled ^{15}N NMR spectra in CD_3OD of [A] 0.020 M $Me_3PAuC^{15}N$, [B] 0.020 M $Et_3PAuC^{15}N$, [C] 0.020 M *i*-$Pr_3PAuC^{15}N$.

The previously recorded[4] K_{eq} values of these complexes are given in Table 2. K_{eq} is different for all complexes under investigation and this suggests that various factors influence K_{eq}. These have been studied by Horman-Arendt and Shaw and include solvent, size of the ligands, initial concentration of complexes, ionic strength of the medium, *etc.*[2,4]

Unfortunately, the ^{15}N chemical shift differences between $Au(C^{15}N)_2^-$ and $R_3PAuC^{15}N$ are very small and not resolved, except for $Et_3PAuC^{15}N$. The

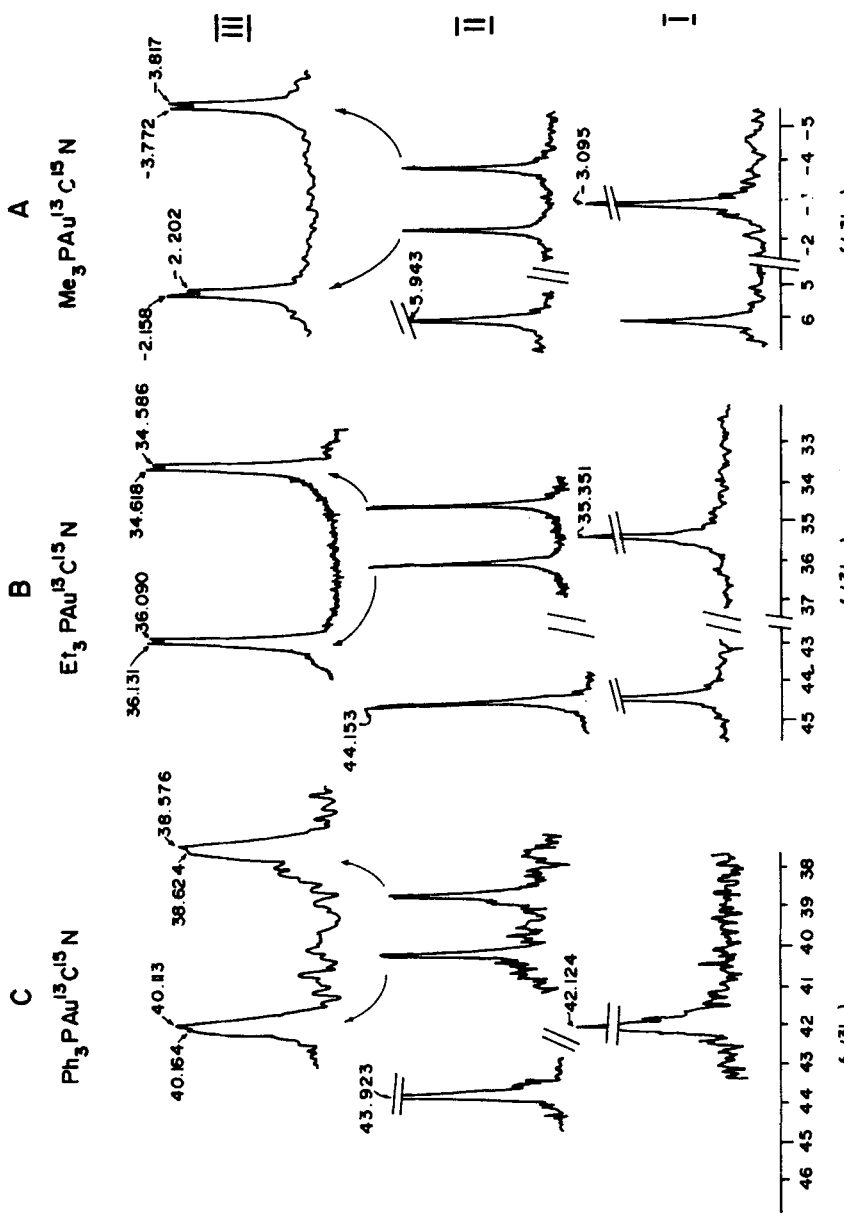

Figure 2 The 109.25 MHz ^{1}H noise-decoupled ^{31}P NMR spectra in CD_3OD of: [A], (I) 0.020 M Me_3PAuCN, (II) 0.020 M $Me_3PAu^{13}C^{15}N$, (III) expanded spectrum of II (all spectra are recorded at 297 K); (B) (I) 0.020 M Et_3PAuCN, (II) 0.020 M $Et_3PAu^{13}C^{15}N$, (III) expanded spectrum of II (all spectra are recorded at 297 K); [C] (I) 0.010 M $Ph_3PAu^{13}C^{15}N$ at 297 K, (II) 0.010 M $Ph_3PAu^{13}C^{15}N$ at 233 K, (III) expanded spectrum of II.

assignment of $Au(C^{15}N)_2^-$ and $Et_3PAuC^{15}N$ resonances is based on the K_{eq} value of the complex,[4] where the $Au(C^{15}N)_2^-$ resonance has to be less intense than that of $Et_3PAuC^{15}N$. The broad ^{15}N resonance for $Me_3PAuC^{15}N$ (Fig. 1A) indicates that $Au(C^{15}N)_2^-$ and $Me_3PAuC^{15}N$ are in slow exchange. However, for *i*-$Pr_3PAuC^{15}N$, the ^{15}N resonance is sharp, indicating fast exchange. For $Ph_3PAuC^{15}N$ (not shown), the exchange-averaged ^{15}N resonance was observed at 265.5 ppm.

Recently, we studied the interaction of $C^{15}N^-$ with gold(I)-thiomalate (Autm) and gold(I)-thioglucose (Autg) in D_2O at pH* 7.40, using ^{15}N NMR which showed the presence of $Au(C^{15}N)_2^-$ and $RSAuC^{15}N^-$ (where RS = tm^- or tg^-) at 265.94 ppm and 260.30 ppm, respectively.[16] It should be noted here that for both tm-$AuC^{15}N^-$ and tg-Au-$C^{15}N^-$ species, the resonances appeared at 260.30 ppm. In the present study, the ^{15}N chemical shift range for all the $R_3PAuC^{15}N$ species is small, between 262.2 to 265.5 ppm in CD_3OD.

As noted in Table 3, ^2J and ^3J values for $Me_3PAu^{13}C^{15}N$ are greater than for

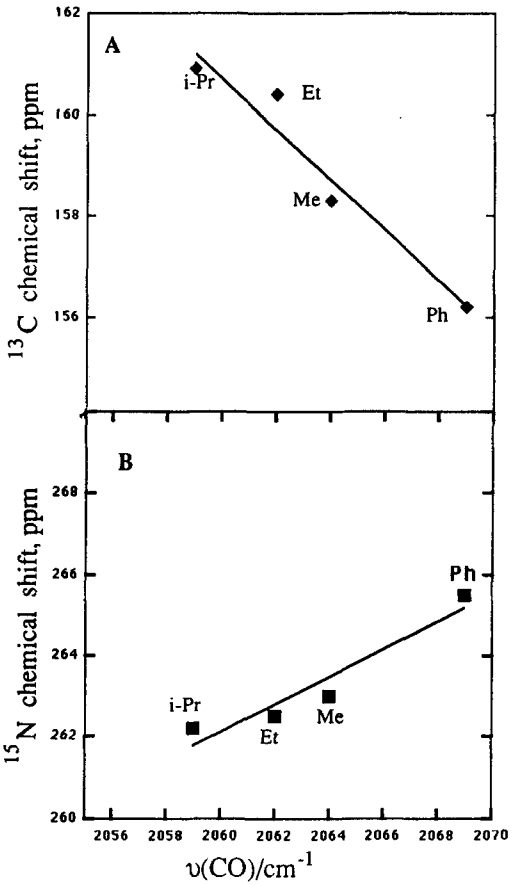

Figure 3 Dependence of the (A) ^{13}C and (B) ^{15}N chemical shifts of $R_3PAu^{13}CN$ (or $R_3PAuC^{15}N$) complexes *vs* ν(CO). The solid lines are regression lines. The ^{13}C chemical shift value are taken from ref. 4 and ν(CO) values from ref. 24.

$Et_3PAu^{13}C^{15}N$ at 297 K; a similar observation was made for $R_3PAu(^{15}N$-phthalimide) (where R = Me, Et, *i*-Pr, Ph, *etc.*) complexes.[23] The magnitude of the ^2J and ^3J coupling constants is expected to reflect the strength of the P-Au bond. For example, increasing the cone angle decreases strength of the P-M bond.

The electronic parameter, ν(CO) for $R_3PNi(CO)_3$, is used by Tollman[24] to demonstrate the relative basicity of phosphines. A decrease in ν(CO) indicates a net increase in the electron-donating ability of a phosphine. Figure 3 shows a linear correlation between ν(CO) *vs* ^{15}N chemical shifts of the $R_3PAuC^{15}N$ complexes. As shown in Table 2 and discussed by Hormann-Arendt and Shaw,[4] it is clear that K_{eq} for the Ph_3PAuCN is less than for alkyl R_3PAuCN complexes. There is an inverse correlation between K_{eq} and ν(CO).[4]

Brown *et al.*[25,26] studied the IR, and ^{13}C and ^{15}N NMR chemical shifts for $^{15}N^{13}CCo(D_2H_2)L$ where L = pyridine, primary amine and 4-substituted aniline and their analogues. Interestingly, $^{15}N^{13}CCo(D_2H_2)L$ and $R_3PAu^{13}C^{15}N$ complexes show an inverse relationship between ^{13}C *vs* ^{15}N NMR chemical shifts (Figures 3 and 4). This could be due to the metal-to-carbon d_π-p_π electron donation, which will lower the charge on the metal; consequently the electron density will be transferred from a filled metal *d*-orbital into the carbon-centred member of the cyanide π*-antibonding orbital. Most of the electron density donated from the metal to the cyanide ligand would be expected to reside on the cyanide carbon, and this would cause a ^{13}C chemical shift down field and an upfield shift of the ^{15}N resonance.

$\Delta G^{\#}$ for the scrambling reaction of Ph_3PAuCN is calculated to be 39.7 ± 0.5 kJ mol^{-1} at 273 K. To the best of our knowledge this is the first $\Delta G^{\#}$ reported for a scrambling reaction described by (*1*). The data presented indicate that ligand

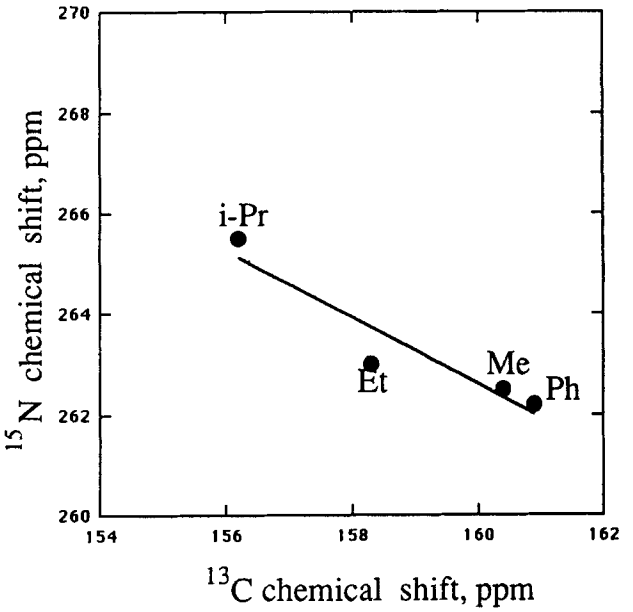

Figure 4 Plot of ^{13}C *vs* ^{15}N chemical shifts of R_3PAuCN complexes. The solid lines are regression lines. The ^{13}C chemical shift values are taken from ref. 4.

scrambling can be followed using ^{15}N NMR spectroscopy. The ^{15}N chemical shift range for $RSAuC^{15}N^-$ and $R_3PAuC^{15}N$ is 260 to 265 ppm in D_2O or CD_3OD. We have also demonstrated linear relationship between ^{15}N chemical shifts of $R_3PAuC^{15}N$ *vs* ν(CO), which shows that when the basicity of phosphines increases the ^{15}N chemical shift also increases.

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