

¹⁵N and ¹³C NMR studies on cyclopalladated complexes. Synthetic palladium cyanide chemistry leading to organic nitriles

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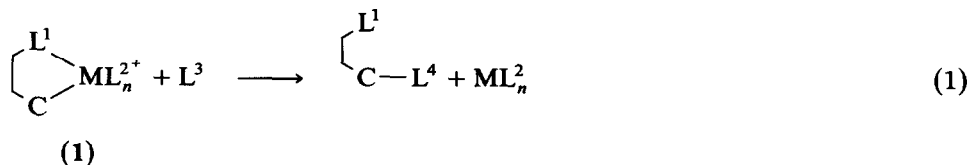
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Abstract

¹⁵N NMR spectroscopy has been used to determine whether the ¹⁵NO group is coordinated in the cyclopalladated nitrosoamine complex [(Pd(μ-OAc)(O=NN-(CH₃)C₆H₄))₂, PdCl{O=NN(CH₃)C₆H₄} {P(OMe)₃} and K₂[Pd(CN)₃(O=NN-(CH₃)C₆H₄)]], **11**, as well as in several platinum(II) analogs. ¹³C NMR studies on **11**, the cyclopalladated *N,N*-dimethylbenzylamine analog K₂[Pd(CN)₃(Me₂NCH₂C₆H₄)]], **12**, and the dicyano cyclopalladated phosphite anion [Pd(CN)₂((PhO)₂P-OC₆H₄)]], **13**, are useful in determining the coordination sphere of these molecules, and afford the novel coupling constants ²*J*(¹³C–Pd–¹³C) *cis* and *trans*, between one cyanide and the palladated carbon. The complexes **11**–**13** are used as models to rationalize the reactions of **11** and **12** with (Bu₄N)CN and diphos to form a 2-cyano-*N*-nitrosoaniline and a 2-cyano-*N,N*-dimethylbenzylamine.

Introduction

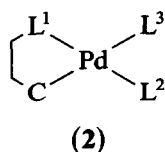
Reactions of cyclometallated complexes to afford organic products, e.g., reaction 1, represent the last step in the transformation of selected monosubstituted aryl



(L⁴ = L³ or modified L³)

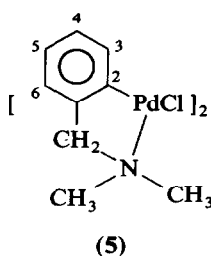
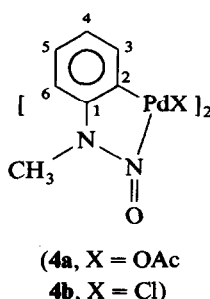
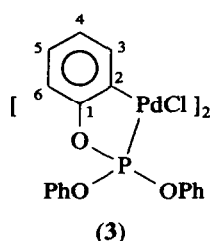
compounds into *ortho*-disubstituted derivatives [1–3]. For complexes of palladium a

number of intermediates, e.g., **2**, have been postulated [3–7] in which L^3 coordinates to the palladium before subsequent transformation to product.



The nature of **2**, i.e., its coordination number, geometry, charge, etc., is important since the insertion of L^3 into a Pd–C bond and/or a reductive elimination step might be readily achieved if the Pd– L^1 bond were labile.

In the course of our synthetic studies on cyclopalladated phosphite [8], nitrosoamine [9], and *N,N*-dimethylbenzylamine [10] ligands, we have found it useful to

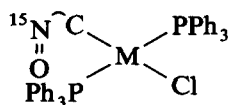


prepare complexes containing enriched ^{15}N ligands, e.g., **4**, with > 95 atom% $^{15}\text{N}=\text{O}$, and/or with enriched (96.8 atom%) $^{13}\text{CN}^-$. These molecules are of interest in that their NMR spectra are rich in structural information and also afford access to relatively rare spin–spin couplings, e.g., $^2J(^{13}\text{C}-\text{M}-^{13}\text{C})$. We report here on the ^{15}N characteristics of several derivatives of **4** and their platinum analogs as well as ^{13}C NMR properties of bis and tris anionic cyano complexes arising from complexes **3–5**.

Results and discussion

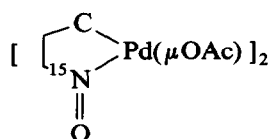
It is useful to abbreviate the cyclometallated ligands and henceforth the cyclometallated species from **3–5** will be written as $\text{O}=\text{N}^-\text{C}$, N^-C and P^-C , respectively, e.g., **4a** = $[\text{Pd}(\mu\text{-OAc})(\text{O}=\text{N}^-\text{C})]_2$.

Complex **4a** can be readily prepared in ca. 90% yield [9] from the enriched ligand and $\text{Pd}(\text{OAc})_2$. Indeed, there are a number of stable cyclopalladated nitrosoamines, and two derivatives of **4b**, $\text{PdCl}(\text{O}=\text{N}^-\text{C})(\text{PPh}_3)$, **6**, and *trans*- $\text{PdCl}(\text{O}=\text{N}^-\text{C})(\text{PPh}_3)_2$, **7**, have been crystallized by Constable et al. [11] and their structures determined.



(7, M = Pd, $\delta^{15}\text{N} = 538.8$

8, M = Pt, $\delta^{15}\text{N} = 546.2$)



(4a, $\delta^{15}\text{N} = 416.6$)

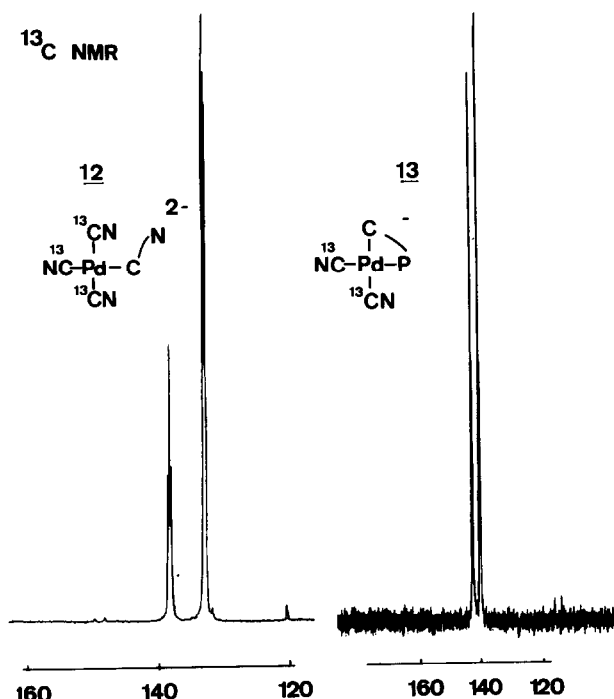
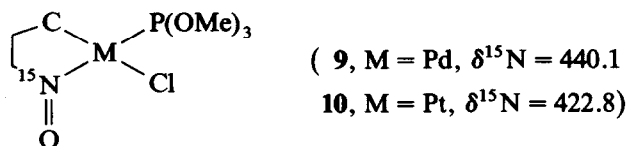


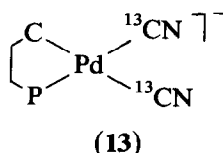
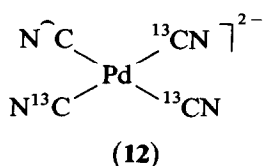
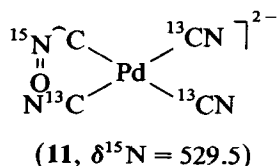
Fig. 1. ^{13}C spectrum of left: complex 12, enriched in $^{13}\text{CN}^-$ and right: ^{31}P NMR spectrum of complex 13, enriched in $^{13}\text{CN}^-$.

The usefulness of the nitrogen-15 chemical shift, $\delta^{15}\text{N}$, in differentiating between coordinated and uncoordinated sp^2 nitrogen atoms has been recognized in the coordination chemistry of azo [12,13], Schiff's base [14], thiocyanate [15], nitrosyl [16–18], diazenido [19] and other ligands [20], and is nicely illustrated by compari-



son of $\delta^{15}\text{N}$ for 4a with $\delta^{15}\text{N}$ for 7, which is known [11] to be the four-coordinate *trans* isomer shown. Complex 7 has an ^{15}N shift of 538.8, close to that of the free ligand, 548.2, whereas complex 4a with bound nitrogen experiences the expected [12–20] large high field (low frequency) shift due to involvement of the nitrogen lone-pair in the palladium nitrogen bond. As we have shown on several occasions [14,21], the magnitude of this high field shift depends on the ligand *trans* to the coordinated nitrogen such that, for sp^2 nitrogen, there is a low field shift with increasing *trans* influence. This effect is illustrated by 9 in which P(OMe)_3 is coordinated *trans* to ^{15}N , relative to 4a with $\mu\text{-OAc}$ *trans* to ^{15}N . Complexes 8 and 10 are platinum analogs of 7 and 9, respectively. The *trans* orientation of the ^{15}N and ^{31}P spins in 9 and 10 is supported by the $^2J(\text{P,N})$ values of 83.5 and 95.2 Hz, respectively, in keeping with earlier reports on this subject [14,15,21–23].

Reaction of either **4a** or **4b** with three equivalents of enriched $^{13}\text{CN}^-$ per palladium affords complex **11**. The ^{15}N resonance, $\delta = 529.5$, is again consistent



with an uncoordinated nitroso function, and in support of this we observe two ^{13}C resonances, a triplet at $\delta = 146.6$ and a doublet at $\delta = 144.6$ in the ratio of 1 : 2, with a $^2J(^{13}\text{C}, ^{13}\text{C})$ value of 7.3 Hz.

The cyclopalladated carbon, C-2, $\delta = 149.2$, is split by the *trans* $^{13}\text{CN}^-$ into a doublet: $^2J(^{13}\text{C}, ^{13}\text{C})_{\text{trans}} = 42.0$ Hz. Although we do not observe a corresponding *cis* coupling, these data seem to support the generally observed [24] trend: $^2J(\text{X}, \text{Y})_{\text{trans}} > ^2J(\text{X}, \text{Y})_{\text{cis}}$.

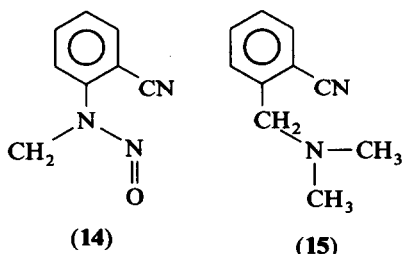
The analogous enriched cyclopalladated *N,N'*-dimethylbenzylamine dianion, $\text{Pd}(^{13}\text{CN})_3(\text{C}^-\text{N}^-)^{2-}$, **12**, also revealed two $^{13}\text{CN}^-$ signals in a 1 : 2 ratio at δ 149.4 and 146.7 with $^2J(^{13}\text{C}, ^{13}\text{C})_{\text{cis}} = 7.0$ Hz, see Fig. 1. The palladated carbon, C-2, $\delta = 154.8$, couples to both $^{13}\text{CN}^-$ ligands, $^2J(^{13}\text{C}, ^{13}\text{C})_{\text{trans}} = 37.6$ Hz and $^2J(^{13}\text{C}, ^{13}\text{C})_{\text{cis}} = 0.5$ Hz, so that in this case the expectation of $^2J_{\text{trans}} > ^2J_{\text{cis}}$ is confirmed. Consequently, we assume that the amine nitrogen is not complexed. For both **11** and **12** the aqueous solutions used for the measurements showed no signs of decomposition over several hours suggesting only a relatively slow reductive elimination possibility. We note that Nast et al. [25] have prepared $(\text{PPh}_4)_2[\text{Pd}(\text{CN})_3\text{Ph}]$.

The cyclopalladated phosphite, **3**, reacts with two equivalents of $^{13}\text{CN}^-$ to afford **13**, in which the phosphite ligand remains bound. In **13** there are two $^{13}\text{CN}^-$ resonances in a 1 : 1 ratio at $\delta = 141.8$ and 135.7 with $^2J(^{31}\text{P}, ^{13}\text{C})$ values of 199 and 21 Hz, respectively, see Fig. 1, thereby allowing the low field signal to be assigned as $^{13}\text{CN}^-$ *trans* to phosphite. The $^2J(^{13}\text{C}, ^{13}\text{C})_{\text{cis}}$ value for the two CN^- ligands is 8.6 Hz. The cyclometallated carbon, C-2, is found at $\delta = 139.6$ with a $^2J(^{31}\text{P}, ^{13}\text{C})$ value of 4.6 Hz. Finally we note that the $^2J(^{13}\text{C}, ^{13}\text{C})_{\text{cis}}$ values in the $\text{Fe}(\text{CN})_5(\text{NO})^{2-}$ dianion and in the $\text{Fe}(\text{CN})_5(\text{NO}_2)^{4-}$ tetraanion are 17.6 and 9 Hz, respectively [26].

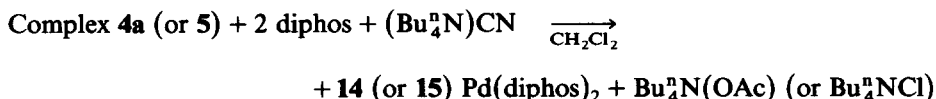
A number of attempts to coordinate an additional CN^- to **13** were essentially fruitless (see Experimental section); however, in one experiment, involving 1 equivalent of **13** and 1 equivalent K^{13}CN in $\text{CDCl}_3/\text{CD}_3\text{OD}$, 1 : 1, the ^{13}C resonance for the cyanide *cis* to phosphite remains visible, but with loss of ^{13}C *cis*-coupling, whereas the ^{13}C resonance for cyanide *trans* to phosphite disappears—as does the ^{13}C signal for the uncoordinated $^{13}\text{CN}^-$ (ca. 164 ppm). It seems that the phosphite ligand labilizes the *trans* position sufficiently to induce a relatively selective CN^- exchange reaction. In the table and Experimental section we give additional supporting data for **7–10** and **11–13**.

We consider the difference in chemistry for **13** relative to **11** and **12** to be of interest in light of the following cyanation reactions:

- Both, **4a** and **5a** react with $(\text{Bu}_4\text{N})\text{CN}$ and diphos, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, to afford reasonable yields of the *ortho* cyano compounds **14** and **15**, respectively.



with the chemistry as shown:



The presence of the Pd(O) complex Pd(diphos)₂ is confirmed by its ³¹P resonance at δ = 32.6. This type of reaction has been reported previously for azobenzene compounds [27].

- (ii) The comparable phosphite chemistry starting from 3 gave no readily detectable nitrile compound (see Experimental section for further comment).

It is possible that the failure to isolate a phosphite analog of 14 or 15 is related to the ease with which CN⁻ coordinates and/or the rate of the presumed subsequent reductive elimination. The coordination is, as we have shown, not so facile for derivatives of 3 as for complexes of 4 and 5. Moreover, since theoretical [28] and experimental work [29] have shown that the reductive elimination from square planar Pd^{II} is facilitated by ligand dissociation, the tendency for the phosphite to remain coordinated could well increase the activation energy for this process as well. In any case, the use of various NMR probes to help in the elucidation of the palladium coordination sphere should prove increasingly valuable for the understanding of these and subsequent transformations involving such metallocycles.

Experimental

NMR spectra were recorded on a Bruker WM-250 and AM-200 spectrometers. Details of the individual measurements are given in Table 1. IR spectra were recorded on a Perkin Elmer 883 spectrophotometer. Mass spectra and elemental analyses were carried out by the analytical laboratory of the ETH Zürich.

Na¹⁵NO₂ and K¹³CN were purchased from Stohler Isotope Chemicals. Complexes 3–5 were prepared by published methods [8–10], as were 7 [7] and 9 and 10 [9]. Complexes 9 and 10 were prepared in 95 and 90% yields, respectively, from their bridging chlorides (see Table 1 for analytical data).

Preparation of 11. The cyclopalladated nitrosoamine 4a (30.6 mg, 0.05 mmol) and K¹³CN (198.8 mg, 0.30 mmol—19.5 mg for the normal KCN reaction) were stirred in 0.5 ml of D₂O. After 30 min the clear solution formed was used for the NMR studies. The IR data were obtained by removal of the D₂O and examination of the resulting solid as a KBr pellet.

Preparation of 12. The cyclopalladated benzylamine 5 (27.6 mg, 0.05 mmol) and K¹³CN (19.8 mg, 0.30 mmol—for the normal KCN reaction 19.5 mg) were stirred in 0.5 ml D₂O. After 30 min the clear solution which resulted was used for the NMR

Table 1. Selected spectroscopic data ^a for 9–15

	9 ^b		10 ^c	
IR, Pd-Cl	247, 291			
³¹ P	117.2		84.3, ¹ J(Pt,P) = 6815	
	¹ H	¹³ C	¹ H	
N-CH ₃	3.60	30.7	3.58 [2.5]	
1		114.2 (3.2)		
2		140.3 (1)		
3	7.67 (6.6)	137.8 (9.6)	7.76 (1.8) [63.8]	
4	7.07	126.6 (6.1)	7.09	
5	7.26	126.3	7.26	
6	7.02	114.0	7.00	
P(OMe) ₃	3.80	53.7 (1.7)	3.86 (12.8) [3.0]	
	11 ^e		12 ^f	
IR ^d	2135, 2116		2110, 2130	
	¹ H	¹³ C	¹ H	¹³ C
N-CH ₃	3.74	38.2	2.34	47.3
CH ₂			3.87	70.7
1		151.1		146.2
2		149.2		154.8
3	7.66	142.6	7.42	140.5
4		130.5		131.5
5		127.5		128.7
6		126.4		126.3
CN		146.6, 144.6		149.4 t, 146.7, d
				141.8 J(P,C) = 199 135.7 J(P,C) = 21
	14 ^h		15	
IR: ν(C≡N)	2226		2228	
ν(N=O)			1460	
ν(N-N)	1081			
	¹ H	¹³ C	¹ H	¹³ C
1		144.5		143.2
2		107.4		112.8
3		134.0 ^j	7.63	132.8 ^j
4		128.6	7.32	127.6 ^j
5		134.4 ^j	7.55	133.0 ^j
6		124.4	7.55	130.3 ^j
CH ₂			3.62	62.0
N-CH ₃	353 ^d	34.4	2.28	45.6
C≡N		116.4		117.8
MS: M ⁺	161. (5.7) ^k		160 (10.5) ^k	

^a δ values in ppm, J values in Hz. Values in parenthesis are couplings to ³¹P, in square brackets, J(Pt,H), CDCl₃. ^b C₁₀H₁₆ClN₂O₄Pd Calcd.: C, 30.13; H, 4.11; N, 6.88; Cl, 8.69. Found: C, 29.93; H, 3.99; N, 6.98; Cl, 8.84. There are ¹⁵N couplings to: NCH₃, 1.75; NCH₃, 1.0; C-1, 6.1; C-2, 0.5; C-5, 0.6; C-6, 2.8. ^c C₁₀H₁₆ClN₂O₄Pt Calcd.: C, 24.26; H, 3.09; N, 5.60; Cl, 7.40. Found: C, 24.51; H, 3.26; N, 5.72; Cl, 7.24. ^d ³J(¹⁵N,CH₃) = 1.6. ^e See ref. 25 for IR of [Pd(Cn)₃(Ph)]⁺. Numbers in parentheses are couplings to ³¹P. ^f D₂O solution, ²J(¹³C,¹³C) for cyanides = 7.3 Hz, ²J(¹³C,¹³C)_{trans} = 42 Hz. H-4–H-6 not resolved. ^g D₂O solution, ¹H resonances of H-4 through H-6 not resolved. ^h ²J(¹³C,¹³C) *trans* and *cis* = 37.6 and 0.5 Hz, respectively. ⁱ CDCl₃ solution, δ³¹P = 142.4 (CD₃OD), 141.1 (CDCl₃) as crown-ether salt. ^j ¹H resonances between 6.55 and 7.40, δ H-3 = 8.08, see text for ²J(¹³C,¹³C) values. ^k There are two isomers of 14 in the ratio 97/3 with NO *cis* to CH₃ as the major component. ^l H–NCH₃ for minor isomer = 4.21 ppm. ^m 7.56, m, 2H; 7.80, m, 2H. ⁿ Tentative assignment. ^o Values in parentheses are relative percentages.

studies. The IR data were obtained by removal of the D₂O and examination of the resulting solid as a KBr pellet.

Preparation of 13. (a) The cyclopalladated phosphite **3** (36 mg, 0.04 mmol), KCN (10.4 mg, 0.16 mmol) and 42.6 mg 18-crown-6 (to solubilize the KCN) were stirred in 2 ml CD₂Cl₂ for 1 h and the resulting clear solution used for the NMR studies. The conversion into **13** is essentially quantitative. (b) Complex **3** (36 mg, 0.04 mmol) and KCN (10.4 mg, 0.16 mmol) were dissolved in 1 ml CD₂Cl₂/CD₃OD, 1:1, and the resulting solution used for NMR studies. The conversion was again quantitative. Removal of the solvent gave a solid from which the IR data were obtained.

Various attempts to coordinate an additional CN⁻ ligand using **13** and CN⁻ in a 1:1 ratio gave the following results:

	CN ⁻ source	Solvent	NMR probe	Result
(i)	(Bu ₄ N)CN	CDCl ₃	³¹ P	only 13 (δ = 142.4) observed
(ii)	K ⁺ CN ⁻ (as 18-crown ether salt)	CDCl ₃	³¹ P	only 13 (δ = 141.1) observed
(iii)	K ⁺ CN ⁻ (as 18-crown ether salt)	CDCl ₃	¹³ C	uncoordinated ¹³ CN (δ = 164.1) observed
(iv)	KCN	CDCl ₃ /CD ₃ OD	³¹ P	only 13 initially observed, slow (hours) alcoholysis
(v)	K ¹³ CN	CDCl ₃ /CD ₃ OD	¹³ C	cyanide exchange, see text.

2-(N-methyl-N-nitrosoamino)benzonitrile, 14. A solution of complex **4a** (120 mg, 0.20 mmol) in ca. 5 ml of CH₂Cl₂ was treated with solid diphos (320 mg, 0.80 mmol). Stirring for 1 h was followed by addition of solid (Bu₄N)CN (108 mg, 0.40 mmol). The mixture was stirred for 3 days at room temperature, the solvent then removed, and the residue repeatedly extracted with 10 ml portions of hexane. The hexane extracts were combined and concentrated under vacuum to give 35 mg (54%) of crude product. An identical procedure starting from 0.20 mmol of **5** afforded 46 mg (72%) of product **15**.

An analogous sequence starting from 180 mg of **3** gave no significant amount of hexane-soluble material. The ³¹P NMR spectrum of the non-hexane soluble fraction showed at least six different components. On the assumption that the phosphite might be coordinated to Pd⁰, basic hydrolysis was attempted, but work-up of the organic products gave no evidence for 2-hydroxybenzonitrile.

N-methyl-N(¹⁵N-nitroso)aniline. To a solution of *N*-methylaniline (4.3 g, 40 mmol) in 6 ml of concentrated HCl with 16 g of ice at 0°C was slowly added a solution of Na¹⁵NO₂ (2.9 g, 40 mmol) in 10 ml of H₂O. Stirring for one hour was followed by extraction of the oily layer with 2 × 50 ml of ether. The ethereal extract was dried (Na₂SO₄) and the solvent removed under vacuum. Fractional distillation of the residue gave 5.2 g (95%) of product.

Acknowledgements

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