Inorg. Chem. 1992, 31, 810–812

Contribution from the Department of Chemistry,
University of California, Riverside, California 92521-0403

Cyanide Exchange of the Methyltricyanoplatinate(II) Dianion: Temporal Resolution of Cis and Trans Cyanide Exchange

Albert Y. C. Hung, John C. Woolcock,[1] Michael F. Rettig,* and Richard M. Wing*

Received August 26, 1991

Square planar anions of the type $[PtR(CN)_3]^{2-}$ have been subjected to exchange with aqueous $^{13}CN^-$ (exchange kinetics followed by ^{13}C NMR). The coordinated alkyl group produces two distinct environments for the coordinated cyanide ligands, which consequently exchange with exogenous CN^- at two different rates. With R = CH_3, **3**, the exchange of cis CN^- is 10^{-3} and trans CN^- is 10^{-7} times slower than the same process for the reference compound $[Pt(CN)_4]^{2-}$. In all these cases the rate laws are strictly second order, first order in CN^- and first in metal complex, with no evidence of a solvent pathway. The slower exchange for the cis cyanides in **3** is predominantly entropy (ΔS^*) controlled, whereas that for the trans cyanide is predominantly enthalpy (ΔH^*) controlled (both compared to $[Pt(CN)_4]^{2-}$). Stabilities of various five-coordinate transition states are calculated and discussed. These systems are particularly unusual in that both cis and trans exchange rates are separately quantitated. There was no indication of cis $\leftrightarrow$ trans isomerization in the absence of exogeneous $^{13}CN^-$; such isomerization in the presence of exogenous $^{13}CN^-$ could not be ruled out as a contributor to incorporation of $^{13}CN^-$ into the trans position.

Introduction

In the course of investigating organoplatinum chemistry with Pt–C σ bonds, we have observed that CN^- treatment of such precursors results in stable, water-soluble complexes of the type $[PtR(CN)_3]^{2-}$.[2] These complexes, whose solution structures are unambiguously established here by ^{195}Pt and ^{13}C NMR spectroscopy, do not lose R nor do their regiospecifically isotopically labeled isomers undergo cis–trans isomerization. The complexes $[PtR(CN)_3]^{2-}$ do, however, undergo ligand exchange with exogenous $^{13}CN^-$ rather slowly and with differential rates for cyanide ligands cis and trans to the R group. These appear to be the first instances in which substitution of both cis and trans ligands on square planar Pt(II) have been quantitatively observed. In contrast, cyanide exchange has been established to be exceptionally rapid[3a] for square planar tetracyanoplatinate(II). Indeed $[Pt(CN)_4]^{2-}$ and the close relatives $[Pd(CN)_4]^{2-}$ and $[Au(CN)_4]^-$ are the ultimate examples of stable yet labile metal complexes.[3a]

We report here the synthesis and kinetic characterization of the lead member of the series of alkyltricyanoplatinates, $[Pt(CH_3)(CN)_3]^{2-}$ (**3**). In contrast to $[Pt(CN)_4]^{2-}$, **3** gives ^{13}C NMR spectra in the presence of exogenous $^{13}CN^-$ which are in the slow-exchange limit, and consequently the monoalkyl systems are readily studied by direct observation of the time course of labeled $^{13}CN^-$ incorporation.

Experimental Section

General Data. ^1H NMR spectra were collected at 300.15 MHz using a GE QE-300 instrument (secondary references δ 4.77 (HDO) in D_2O or δ 7.27 ($CHCl_3$) in $CDCl_3$ vs TMS* or TMS, respectively). ^{13}C NMR spectra were recorded at 75.48 MHz with the QE-300 (secondary reference δ 165.0 for free CN^- in D_2O vs TMS*). The spectral assignments were straightforward.

Infrared spectra were obtained on a Nicolet 5DX FT-IR spectrometer by evaporation of aqueous solutions to form solid **3**, followed by formation of a Fluorolube mull on KBr. Reagent grade chemicals and solvents, including $CDCl_3$ and D_2O, were purchased from Aldrich or Fisher Scientific. Enriched 99% ^{13}C-enriched sodium cyanide was purchased from Stohler Isotope Chemicals. Zeise's dimer, *trans*-$[(\mu\text{-Cl})Pt(Cl)(C_2H_4)]_2$ (**1**), was prepared by a literature procedure.[4]

Synthesis and Characterization of *trans*-$[(\mu\text{-Cl})Pt(CH_3)(C_2H_4)]_2$ (2). Dimer **2** was prepared by methylation of Zeise's dimer, **1**, with Me_4Sn in the presence of excess ethylene. Compound **1** (109.7 mg, 0.185 mmol) was dissolved in 4 mL of dichloromethane. The resultant yellow orange solution was degassed with He for 5 min, saturated with ethylene, and cooled to 0 °C in an ice bath. Tetramethyltin (0.51 mL, 0.370 mmol) was added dropwise over a period of 5 min until addition of the tin reagent was complete. The yellow solution (with a tiny amount of pale yellow precipitate) was stirred 30 min longer with excess ethylene and with maintainance of the temperature at 0 °C, resulting in a clear yellow solution. After 30 min of standing at room temperature, the solution was chromatographed on a small Florisil column using CH_2Cl_2 as eluent to remove various organotin impurities. A pale brown fraction was collected and freed from solvent in vacuo. Recrystallization from dichloromethane/hexane gave 52 mg (51% yield) of **2**. ^1H NMR of **2** (ppm), in $CDCl_3$: δ 0.60 (s, $^2J_{Pt-H}$ = 81 Hz, Pt–CH_3), 3.78 (s, $^2J_{Pt-H}$ = 80 Hz, C_2H_4).[4]

Table I. Rate Data for Cis CN^- Exchange Reaction

$[Pt(CH_3)(CN)_3]^{2-}$, M	$[^{13}CN^-]$, M	T, °C	10^6R_{ex}, M s^{-1}	$10^3k_{2,c}$, M^{-1} s^{-1}
0.004 28	0.1027	1.7	4.5	10.2
0.008 56	0.2056	1.6	17.3	9.8
0.008 56	0.2056	6.7	19.2	10.9
0.008 56	0.2056	11.5	21.0	11.9

Table II. Rate Data for Trans CN^- Exchange Reaction

$[Pt(CH_3)(^{13}CN)_2(CN)]^{2-}$, M[a]	$[^{13}CN^-]$, M	T, °C	10^9R_{ex}, M s^{-1}	$10^6k_{2,t}$, M^{-1} s^{-1}
0.008 490	0.1885	24.0	4.2	2.6
0.008 490	0.1885	40.0	14.3	8.9
0.008 490	0.1885	50.0	29.1	18.2
0.004 245	0.0941	50.0	7.3	18.2

[a] The two $^{13}CN^-$ groups are cis to the methyl group.

Disodium Methyltricyanoplatinate(II), $Na_2[Pt(CH_3)(CN)_3]$ (3). *Caution! Cyanide is toxic!* In a screw cap vial, dimer **2** (50 mg, 0.09 mmol) was dissolved in 4.0 mL of $CDCl_3$ and 3 equiv of NaCN (per Pt) in D_2O was added. The resulting two-layer system was shaken for 5 min, during which time the yellow color disappeared from the organic layer. After separation the aqueous fraction (which was analyzed quantitatively by ^1H NMR spectroscopy using internal reference acetone) yielded 0.079 mmol (87%) of **3**. The corresponding ^{13}C-labeled complex $Na_2[Pt(CH_3)(^{13}CN)_3]$ (**4**) was prepared as above except for the use of 99% ^{13}C-labeled sodium cyanide. NMR of **4**: See Table IV. IR of **3** (cm^{-1}): 2134 ($A_1^{(1+2)}$), 2103 (B_2 and $A_1^{(1-2)}$).

Kinetic data were obtained by integration of the ^{13}C resonances corresponding to coordinated $^{13}CN^-$ cis or trans to CH_3 as appropriate. The sample temperatures were maintained at ±0.2 °C of those stated using the thermostated probe provided with the NMR spectrometer or in case of the slow high-temperature reactions by thermostating sealed tubes in a Fisher Scientific Isotemp Immersion Circulator Model 730 temperature bath. In the latter case the tubes were assayed at room temperature at appropriate ca. 3–12-h intervals. A typical ^{13}C NMR spectrum required about 30 min to accumulate. Since this system is a classical example of exchange approach to equilibrium with an equilibrium constant of unity, we used McKay's analysis[5] to extract the apparent rate of exchange from

---

(1) Present address: Department of Chemistry, Indiana University of Pennsylvania, Indiana, PA 15705.

(2) Similar Pd(II) complexes were described earlier in another context: (a) Parra-Hake, M.; Rettig, M. F.; Wing, R. M.; Woolcock, J. C. *Organometallics* **1982**, *1*, 1478–1480. (b) Isolation of solid $[K(18\text{-crown-}6)]_2[RPt(CN)_3]$: Almeida, J. F.; Pidcock, A. *J. Organomet. Chem.* **1981**, *208*, 273–278.

(3) (a) Pesek, J. J.; Mason, W. R. *Inorg. Chem.* **1983**, *22*, 2958–2959. (b) Pesek, J. J.; Mason, W. R. *Inorg. Chem.* **1979**, *18*, 924–928.

(4) Scott, J. D.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1984**, 193.

(5) (a) McKay, H. A. C. *J. Am. Chem. Soc.* **1943**, *65*, 702. (b) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill Book Co.: New York, 1981; Chapter 3.

0020-1669/92/1331-0810$03.00/0

the raw data. The time course data were used to generate apparent first-order rate constants, which are given in Tables I and II. The true rate constants are overall second order, first order both in CN$^-$ and in complex. The exchange constants $k_{2,c}$ or $k_{2,t}$ are given in the last column of Tables I and II. Samples for determination of the trans exchange rates were, as a consequence of the large differential in rates, fully equilibrated solutions from the cis exchange process.

Results and Discussion

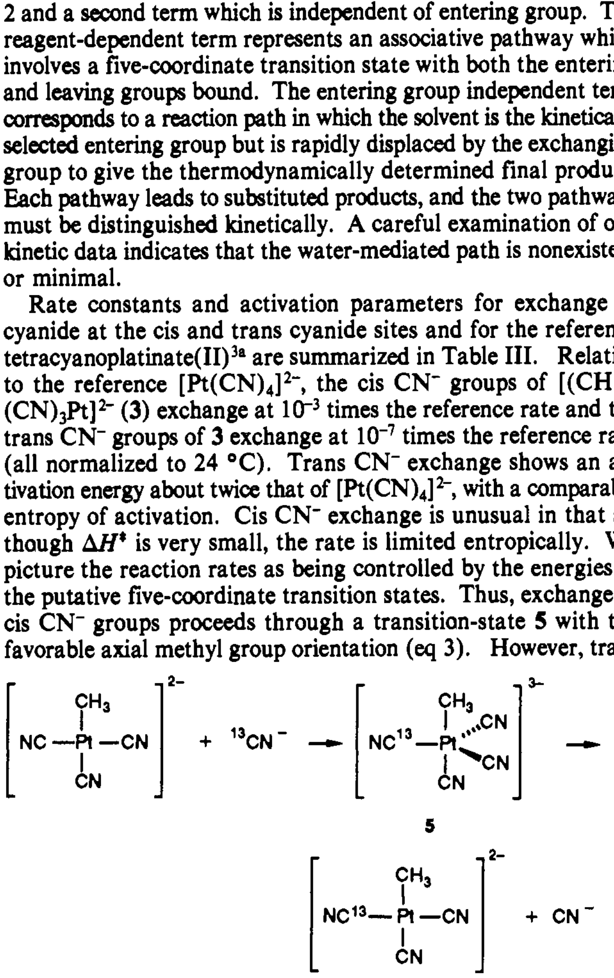
The CN$^-$ exchange rate data are consistent with eq 1 for cis CN$^-$ exchange and eq 2 for trans CN$^-$ exchange.

$$\text{rate} = k_{2,c}([Pt(CH_3)(CN)_3]^{2-})[^{13}CN^-] \qquad (1)$$

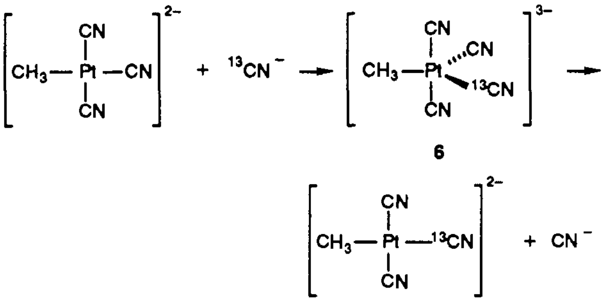
$$\text{rate} = k_{2,t}([Pt(CH_3)(^{13}CN)_2(CN)]^{2-})[^{13}CN^-] \qquad (2)$$

Square planar substitution reactions are believed to proceed by two pathways.[3a,6] Thus the general rate law consists of a term that depends on the substituting reagent analogous to eqs 1 or 2 and a second term which is independent of entering group. The reagent-dependent term represents an associative pathway which involves a five-coordinate transition state with both the entering and leaving groups bound. The entering group independent term corresponds to a reaction path in which the solvent is the kinetically selected entering group but is rapidly displaced by the exchanging group to give the thermodynamically determined final product. Each pathway leads to substituted products, and the two pathways must be distinguished kinetically. A careful examination of our kinetic data indicates that the water-mediated path is nonexistent or minimal.

Rate constants and activation parameters for exchange of cyanide at the cis and trans cyanide sites and for the reference tetracyanoplatinate(II)[3a] are summarized in Table III. Relative to the reference $[Pt(CN)_4]^{2-}$, the cis CN$^-$ groups of $[(CH_3)(CN)_3Pt]^{2-}$ (**3**) exchange at 10^{-3} times the reference rate and the trans CN$^-$ groups of **3** exchange at 10^{-7} times the reference rate (all normalized to 24 °C). Trans CN$^-$ exchange shows an activation energy about twice that of $[Pt(CN)_4]^{2-}$, with a comparable entropy of activation. Cis CN$^-$ exchange is unusual in that although ΔH^* is very small, the rate is limited entropically. We picture the reaction rates as being controlled by the energies of the putative five-coordinate transition states. Thus, exchange of cis CN$^-$ groups proceeds through a transition-state **5** with the favorable axial methyl group orientation (eq 3). However, trans exchange requires that, in the transition-state **6**, the methyl group be placed in the trigonal plane as shown in eq 4. Transition-state **6** is energetically unfavorable since, while CH$_3$ is an excellent σ donor (no doubt accounting for the overall slower associative exchange rates[7,8] compared to $[Pt(CN)_4]^{2-}$), it is not a π acceptor.[6b,12] Indeed the σ donor strength of CH$_3$ is clearly reflected in the Pt–C coupling constants ($^{13}CN^-$ trans to R) of Table IV, which show that methyl has an advantage even over CN$^-$.[9] Consistent with this trend is that the tertiary carbon donor η^1-(*C*5)-5-benzylcyclooct-1-en-5-yl weakens the σ interaction with a trans CN$^-$ ligand even more than methyl. Note that for both R groups the ground-state platinum–carbon couplings (J_{Pt-C}) observed (***trans influence***) suggest that trans exchange would be the fastest of all the possibilities. Clearly the π-bonding contribution to the ***trans effect*** dominates the relative rates.



(3)



(4)

Table III. Rate Constants and Activation Parameters

reacn	k_2(24 °C), M^{-1} s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}
$[Pt(CN)_4]^{2-} + {}^{13}CN^- \xrightarrow{k_2}$	26	22 ± 2^b	-143 ± 5
$[Pt(CH_3)(CN)_3]^{2-} + {}^{13}CN^- \xrightarrow{k_{2,c}}$	$1.49 \times 10^{-2\,a}$	9 ± 1^c	-249 ± 5
$[trans\text{-}Pt(CH_3)(^{13}CN)_2(CN)]^{2-} + {}^{13}CN^- \xrightarrow{k_{2,t}}$	$2.61 \times 10^{-6\,a}$	57.3 ± 0.1^d	-160 ± 4

[a] Taken from Arrhenius plots. [b] E_a = 26 kJ mol^{-1} from ref 3a. [c] E_a = 12.6 kJ mol^{-1}. [d] E_a = 59.5 kJ mol^{-1}.

The putative single point (not geometry optimized) five-coordinate transition states [calculated for Ni(II) rather than Pt(II)] were compared computationally[10] using the STO3-21G basis set and the program SPARTAN.[11] Since the results for the methyl complex were so promising, we proceeded to the *tert*-butyl derivative and the hypothetical *p*-nitrophenyl compound (Table V). Indeed our preliminary experimental kinetic study[13] of $[\eta^1\text{-(5-benzylcyclooct-1-en-5-yl)}(CN)_3Pt]^{2-}$ (a *tert*-butyl analogue) indicates a much more differentiated rate with the pair of cis CN$^-$'s equilibrating with added $^{13}CN^-$ within 1 min and the trans CN$^-$ still untouched after 6 weeks at room temperature. Indeed this larger separation of rates represents more the norm for ligand exchange on square planar platinum(II). We suggest (Table V) that an aromatic derivative such as *p*-nitrophenyl would result in a system with minimal selectivity.

Why the entropic limitation for cis CN$^-$ exchange? By placement of the CH$_3$ group in the axial position, **5**, the transition state is highly restricted compared to possibilities in the case of $[Pt(CN)_4]^{2-}$. In the latter case in addition to the multiple equivalent trigonal bipyramids there is arguably an equally rich manifold of square pyramids which can be arrived at directly or by sequences of pseudorotations. Thus, we expect the exchange

---

(6) (a) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1967; Chapter 5. (b) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole Publishing Co.: Monterey, CA, 1985; Chapter 2.

(7) Mink, L.; Rettig, M. F.; Wing, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 2065–2071.

(8) The positive charge on the (nickel) center was calculated for $[Ni(CN)_4]^{2-}$, 1.223; $[(tert\text{-butyl})Ni(CN)_3]^{2-}$, 1.133; and $[CH_3Ni(CN)_3]^{2-}$, 1.079 (see refs 9 and 10 for details).

(9) An extensive discussion of cis and trans influences of CN$^-$ ligands based on ^{195}Pt and ^{13}C NMR spectroscopy has been given by: Appleton, T. G.; Hall, J. R.; Williams, M. A. *Aust. J. Chem.* **1987**, *40*, 1565–1579. We are not in total agreement with them; however, their emphasis is on Pt(IV) and ours is on Pt(II).

(10) We thank Silicon Graphics for the loan of a Personal Iris 4D25TG computer, which was used to calculate relative transition-state energies using SPARTAN and the STO3-21G basis set.

(11) Spartan, Wavefunction, Inc., Suite 210, 1840 Von Karman Avenue, Irvine, CA 92715. Single point calculations on trigonal bipyramids were based on the following geometric parameters: CN = 1.160 Å, Ni–*ax*-CN = 1.84 Å, and Ni–*eq*-CN = 1.94 Å. The square pyramid had Ni–*ax*-CN = 2.17 Å, Ni–*eq*-CN = 1.87 Å, and the ax–Ni–eq angle = 100.5° Add 0.07 Å to the nickel–carbon distance for aliphatic carbon and 0.04 Å for aromatic carbon. See ref 12 for a discussion of the methods and limitations of doing calculations on platinum-containing systems.

(12) Lin, Z.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 646–651.

(13) Aqueous $[\eta^1\text{-(5-benzylcyclooct-1-en-5-yl)}(CN)_3Pt]^{2-}$ is obtained by treatment of the *sp*-Pt(II) precursor[14] with aqueous cyanide (procedure similar to that for **3**).

(14) Rakowsky, M. H.; Woolcock, J. C.; Rettig, M. F.; Wing, R. M. *Organometallics* **1988**, *7*, 2149–2158.

Table IV. NMR Data For $[Pt(CN)_4]^{2-}$, $[Pt(CH_3)(^{13}CN)_3]^{2-}$, and $[Pt(R)(CN)_3]^{2-}$[a]

param	$[Pt(CN)_4]^{2-}$[b,c]	$[Pt(CH_3)(^{13}CN)_3]^{2-}$[c]	$[Pt(R)(CN)_3]^{2-}$[c]
$^1J_{Pt-C}$ (cis $^{13}CN^-$), Hz	1034[e]	1107	1210
$^1J_{Pt-C}$ (trans $^{13}CN^-$), Hz	1034[d]	721	613
$^1J_{Pt-CH_3}$, Hz		466	
$^2J_{Pt-H}$, Hz		65.7	
$^2J_{CN,CN}$ (cis and trans), Hz		4.5	5.2
$^3J_{CH}$ (cis and trans CN–CH_3), Hz		2	
δ_C (cis $^{13}CN^-$), ppm	125.7 (s)	138.9 (d)	142.8 (d)
δ_C (trans $^{13}CN^-$), ppm	125.7 (s)	144.3 (t)	143.7 (t)
δ_C (Pt–CH_3), ppm		−19.3 (s, obsd only for unlabeled **3**)	
δ_H (CH_3), ppm		0.31 (q)	
$\delta_{^{195}Pt}$, ppm	−4770[f]	−4574[d] (1:2:1 triplet of doublets, $^1J_{Pt-C}$ 1107 and 721 Hz as above, 99% $^{13}CN^-$ sample)	−4376[d] (s, $\Delta\nu_{1/2} \sim 170$ Hz, natl abundance $^{13}CN^-$) and −4378 (m, 1:2:1 triplet of doublets, $^1J_{Pt-C}$ 1210 and 613 Hz as above, 99% $^{13}CN^-$ sample)

[a] R is η^1-(5-benzylcyclooct-1-en-5-yl). C5 is σ-bonded to Pt(II); see ref 13. [b] From ref 3b. [c] Letters in parentheses are multiplicities. [d] From ^{195}Pt NMR (this work), ppm value is set with $[PtCl_6]_{aq}^{2-}$ at δ 0.0. [e] Brown, F.; Heaton, B. T.; Sabounchei, J. *J. Organomet. Chem.* **1977**, *142*, 413. [f] Pesek, J. J.; Mason, W. R. *J. Magn. Reson.* **1977**, *25*, 519.

Table V. Trigonal Bipyramidal Model for CN^- Exchange Transition State Using the 3-21G Basis Set

substituent orientation	energy, hartree		
	Me	*t*-Bu	*p*-nitrophenyl
axial	−1905.80273	−2022.27245	−2297.63435
equatorial	−1905.78669	−2022.24088	−2297.62392
differential activation energy (DDH*)[a]	42 kJ mol^{-1}	83 kJ mol^{-1}	27 kJ mol^{-1}

[a] Axial position for methyl is favored (i.e. CN^- is superior to R as trans director).

process with the single unique transition-state **5** to be slowed for entropic (probabilistic) reasons. Indeed the very large ΔS^* difference of ~110 J K^{-1} mol^{-1} ($[Pt(CN)_4]^{2-}$ vs cis **3**) strongly suggests involvement of both five-coordinate geometries in the transition state for $[Pt(CN)_5]^{3-}$ because only about 20 J K^{-1} mol^{-1} can be explained by postulating a single transition-state geometry.

The ΔS^* value for trans exchange in **3** is in the normal range. We assert that the transition-state **6** must be much closer to square pyramidal geometry than to the trigonal bipyramidal geometry assumed for **5**. The square pyramid geometry is easily achieved via pseudorotation, and with the addition of this geometry (methyl group along the 4-fold axis) the transition-state symmetry number will closely approach that for $[Ni(CN)_5]^{3-}$. Of course for this case of square pyramidal transition-state geometry, trans exchange will be indistinguishable from cis–trans isomerization. We have carefully checked and find no evidence for pure cis–trans isomerization in the *absence* of exogenous CN^-. The absence of cis–trans isomerization is not surprising because such isomerizations are generally base- or ligand-catalyzed and in the presence of excess CN^- the fact of the 10^4 differential in rates will remove any evidence of the unsymmetrically labeled product. Therefore we cannot distinguish between pure trans exchange and cis–trans isomerization but can only set an upper limit on the rate of the former. It is important to note that the conversion of the trigonal bipyramid to a square pyramid structure will be favored if the methyl group (due to its strong σ donor vs weak π acceptor nature) takes a trigonal rather than axial position in the trigonal bipyramid. The possibility of a square pyramidal transition state has been checked by calculation[10,11] and certainly seems reasonable (e.g. only *9* kJ mol^{-1} above the trigonal bipyramid). Also, the near isoenergetic relationship between square pyramids and trigonal bipyramids is evident in the crystal structure[15] of $[Ni(CN)_5]^{3-}$. We calculate at the same level of theory that the square pyramid is favored by 17 kJ mol^{-1} in the $[Ni(CN)_5]^{3-}$ system.

In closing we assert that the large differential rate of exchange for **3** and the lack of unsymmetrically labeled product during the first exchange process constitutes proof of trigonal bipyramidal geometry in the transition state for CN^- exchange at the cis sites. Equally interesting is the fact that the relative difference in lability of CN^- in the two environments is small vis-a-vis most square planar Pt(II) systems (where only *one* substitution step is normally observed) and that there is a prospect of reducing the difference in rates even more by replacing the alkyl group with a properly chosen aryl group (e.g. *p*-nitrophenyl).

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We also thank the University of California Committee on Research for partial financial support. We thank Dr. George Wiger for a gift of $Na^{13}CN$ and Dr. Dan Borchardt for the assistance with low-temperature NMR experiments. We thank a reviewer for bringing ref 9 to our attention.

---

(15) Raymond, K. N.; Corfield, P. W. R.; Ibers, J. *Inorg. Chem.* **1968**, *7*, 1362–1377.