

existence of  $\text{Mn}(\text{CO})_6^{2+}$  is not a consequence of reduced  $\sigma$ -donating ability of carbonyl but rather is a result of the much greater HOMO stabilization in the carbonyl parent species with a resultant increased difficulty of oxidation.

A careful examination of our calculations indicates that the origin of the HOMO stabilization lies in the electron distributions within the ligand moieties. In the series, the electron population on a carbonyl carbon atom is less than that on the carbon atom of the methyl isocyanide adjacent to the metal. Consequently, the carbonyl carbon atoms carry greater positive charges than do their methyl isocyanide counterparts. Such positive charges in proximity to the transition metal have a stabilizing effect upon its 3d electrons and the resultant HOMO. Thus, the positive charge stabilization is not a direct one in the sense of having a higher charge on the metal but is indirect, through its near-neighbor interactions. Identification of this phenomenon is particularly relevant since there are computational methods in the literature which do not include such interactions in their calculational procedure.

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**Registry No.**  $\text{Mn}(\text{CO})_6^+$ , 21331-06-6;  $\text{Mn}(\text{CO})_5(\text{CNCH}_3)^+$ , 45113-87-9;  $\text{Mn}(\text{CO})_4(\text{CNCH}_3)_2^+$ , 45146-17-6;  $\text{Mn}(\text{CO})_3(\text{CNCH}_3)_3^+$ , 45167-07-5;  $\text{Mn}(\text{CO})_2(\text{CNCH}_3)_4^+$ , 45186-22-9;  $\text{Mn}(\text{CO})(\text{CNCH}_3)_5^+$ , 45211-82-3;  $\text{Mn}(\text{CO})_5\text{Br}$ , 14516-54-2;  $\text{Mn}(\text{CO})_4(\text{CNCH}_3)\text{Br}$ , 39048-79-8;  $\text{Mn}(\text{CO})_3(\text{CNCH}_3)_2\text{Br}$ , 38833-18-0;  $\text{Mn}(\text{CO})_2(\text{CNCH}_3)_3\text{Br}$ , 39043-33-9;  $\text{Mn}(\text{CO})(\text{CNCH}_3)_4\text{Br}$ , 38833-19-1;  $\text{Fe}(\text{CNCH}_3)_6^{2+}$ , 17455-63-9;  $\text{Mn}(\text{CNCH}_3)_6^+$ , 45228-39-5;  $\text{Mn}(\text{CO})_5\text{CN}$ , 15602-37-6;  $\text{Mn}(\text{CN})_6^{5-}$ , 19567-57-8;  $\text{CNCH}_3$ , 593-75-9.

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## The Ylide-Metal Complex. Preparations and Structures of Palladium(II) Complexes with a Stable Sulfur or a Nitrogen Ylide

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Palladium(II) complexes with a stable sulfur ylide,  $\text{PdCl}_2\text{L}(\text{Scy})$ ,  $\text{Pd}_2\text{Cl}_4(\text{PPhMe}_2)_2(\text{Scy})$ , and  $\text{PdCl}_2(\text{Scy})_2$  [ $\text{L} = \text{PPh}_3$ ,  $\text{PPh}_2\text{Me}$ ,  $\text{AsPh}_3$ ;  $\text{Scy} = (\text{CH}_3)_2\text{SC}(\text{CN})_2$ ], and with a nitrogen ylide,  $\text{PdCl}_2\text{L}(\text{Ncy})$  and  $\text{Pd}_2\text{Cl}_4(\text{Ncy})_2$  [ $\text{L} = \text{PPh}_3$ ,  $\text{PPh}_2\text{Me}$ ,  $\text{PPhMe}_2$ ;  $\text{Ncy} = 3\text{-CH}_3\text{C}_5\text{H}_4\text{NC}(\text{CN})_2$ ], were prepared. Three types of coordination sites were found in  $\text{Scy}$ ;  $\text{Scy}$  acts as a monodentate ligand through one nitrile group and the dimethylsulfonium sulfur and as a bidentate one through two nitrile groups to give the  $\text{Scy}$ -bridged dimer. The configurations of the complexes are elucidated on the basis of the analogy of  $\text{Scy}$  to tricyanomethanide anion and dimethyl sulfoxide. The difference of nucleophilicity between  $\text{Scy}$  and  $\text{Ncy}$  is discussed from their structures.

### Introduction

To date, several publications have reported the reactions of various ylides with transition metal compounds, especially metal carbonyls, which are of interest in organometallic and organic reactions.<sup>1-8</sup> These studies primarily concern the use of ylides as a substrate in organometallic reactions. On the other hand, there have been few reports on metal complexes with ylides as ligand molecules.<sup>9-12</sup> Recently, we prepared some palladium(II) and platinum(II) halide complexes with stable sulfonium phenacylide  $\text{CH}_3(\text{C}_6\text{H}_5)\text{SCHC}(\text{O})\text{C}_6\text{H}_4\text{Cl}$ -*p* and discussed the bonding character of the metal-ylide carbon bond.<sup>13</sup> The  $\text{Scy}$  and  $\text{Ncy}$  ylides used in the present study involve two cyano groups, which have more electron-

withdrawing power than the carbonyl in the phenacylide, and therefore they are expected to be less reactive at the ylide carbon.

This paper reports the isolation of palladium(II) complexes with  $\text{Scy}$  and  $\text{Ncy}$  and their configurations. The nucleophilicity of these ylides is also discussed.

### Experimental Section

Dimethylsulfonium dicyanomethylide,  $(\text{CH}_3)_2\text{SC}(\text{CN})_2$  ( $\text{Scy}$ ),<sup>14</sup> and 3-methylpyridinium dicyanomethylide,  $3\text{-CH}_3\text{C}_5\text{H}_4\text{NC}(\text{CN})_2$  ( $\text{Ncy}$ ),<sup>15</sup> were prepared according to the literature.

All manipulations for preparing the ylide complexes were carried out in air.

**Preparation of  $\mu$ -(Dimethylsulfonium dicyanomethylide)-bis(di-**

Table I. Melting Point, Elemental Analysis, and Molecular Weight of the Ylide Complexes

Complex	Mp, °C	% C		% H		% N		Mol wt <sup>a</sup>	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Scy	102–103 <sup>b</sup>	47.59	47.53	4.79	4.75	22.20	21.57		
PdCl <sub>2</sub> (Scy) <sub>2</sub>	>145 dec	27.95	28.20	2.82	2.79	13.04	13.06		
PdCl <sub>2</sub> (PPh <sub>3</sub> )(Scy)	>169 dec	48.83	48.97	3.74	3.73	4.95	5.00	566	527
PdCl <sub>2</sub> (PPh <sub>2</sub> Me)(Scy)	>170 dec	42.92	42.88	3.80	3.89	5.56	5.64	504	434
Pd <sub>2</sub> Cl <sub>4</sub> (PPhMe <sub>2</sub> ) <sub>2</sub> (Scy)	>152 dec	33.32	33.16	3.73	3.86	3.70	3.83	757	491
PdCl <sub>2</sub> (AsPh <sub>3</sub> )(Scy)·CHCl <sub>3</sub>	>140 dec	39.54	39.40	3.04	3.19	3.84	4.03		
Ncy	211–212 <sup>c</sup>	68.78	68.72	4.49	4.22	26.73	26.64		
Pd <sub>2</sub> Cl <sub>4</sub> (Ncy) <sub>2</sub>	>175 dec	32.32	32.34	2.11	2.23	12.56	11.89		
PdCl <sub>2</sub> (PPh <sub>3</sub> )(Ncy)	>207.5 dec	54.34	54.23	3.72	3.77	7.04	7.00	597	478
PdCl <sub>2</sub> (PPh <sub>2</sub> Me)(Ncy)	>168 dec	49.42	49.04	3.77	3.73	7.86	7.99	535	437
PdCl <sub>2</sub> (PPhMe <sub>2</sub> )(Ncy)	>111 dec	43.20	43.07	3.84	3.81	8.89	9.05	473	405

<sup>a</sup> In chloroform. <sup>b</sup> Lit.<sup>14</sup> 100–101°. <sup>c</sup> Lit.<sup>15</sup> 214°.

**methylphenylphosphine)tetrachloropalladium(II).** A 15-ml dichloromethane solution of Scy (0.16 g, 1.3 mmol) was added to a 15-ml dichloromethane solution of bis(dimethylphenylphosphine)-dichloro- $\mu,\mu'$ -dichloro-palladium(II) (0.40 g, 0.64 mmol), and the mixture was stirred for 1.5 hr. The addition of petroleum ether to the solution gave orange needles (0.34 g, yield 71%).

Dichloro(methyldiphenylphosphine)(dimethylsulfonium dicyanomethylide)palladium(II) and dichloro(dimethylphenylphosphine)(3-methylpyridinium dicyanomethylide)palladium(II) were synthesized by the same way.

**Preparation of Dichlorotriphenylphosphine(dimethylsulfonium dicyanomethylide)palladium(II).** A suspension of bis(triphenylphosphine)dichloro- $\mu,\mu'$ -dichloro-palladium(II) (0.29 g, 0.33 mmol) and Scy (0.18 g, 1.4 mmol) in acetonitrile (100 ml) was refluxed for 4 hr to give an almost clear solution. The solution was concentrated to about half-volume under reduced pressure and filtered. The addition of diethyl ether to the filtrate gave reddish orange crystals (0.18 g, yield 48%).

Dichlorotriphenylarsine(dimethylsulfonium dicyanomethylide)-palladium(II) and dichlorotriphenylphosphine(3-methylpyridinium dicyanomethylide)palladium(II) were synthesized similarly, but the former was obtained from a chloroform–benzene solution as brown crystals.

**Preparation of Dichlorobis(dimethylsulfonium dicyanomethylide)palladium(II).** To a suspension of bis(benzonitrile)dichloro-palladium(II) (0.30 g, 0.78 mmol) in acetonitrile (5 ml) a 10-ml acetonitrile solution of Scy (0.40 g, 3.2 mmol) was added. The mixture was refluxed for 2.5 hr and evaporated to half-volume under reduced pressure, and a 1:1 mixture of dichloromethane and petroleum ether was added to the solution to give yellow crystals (0.11 g, yield 33%).

**Preparation of Dichloro(methyldiphenylphosphine)(3-methylpyridinium dicyanomethylide)palladium(II).** A 10-ml 1,2-dichloroethane solution of Ncy (0.14 g, 0.87 mmol) was gradually dropped into a suspension of bis(methyldiphenylphosphine)dichloro- $\mu,\mu'$ -dichloro-palladium(II) (0.30 g, 0.40 mmol) in 1,2-dichloroethane (10 ml) to give an orange solution. After refluxing for 1 hr, the solvent was removed under reduced pressure to produce an oil, which was dissolved in dichloromethane. The addition of petroleum ether to the solution gave an orange-yellow powder (0.20 g, yield 47%).

**Preparation of Bis(3-methylpyridinium dicyanomethylide)dichloro- $\mu,\mu'$ -dichloro-palladium(II).** To a solution of bis(benzonitrile)dichloropalladium(II) (0.30 g, 0.78 mmol) in 10 ml of dichloromethane was mixed Ncy (0.26 g, 1.6 mmol) in dichloromethane (20 ml) with stirring to give a brown precipitate. The mixture was further stirred for 4 hr. The product was separated by filtration, washed with dichloromethane and then diethyl ether, and dried *in vacuo* (0.11 g, yield 42%).

The melting points and analytical data for the ylides and their complexes are listed in Table I.

**Physical Measurements.** Ir (4000–200 cm<sup>-1</sup>) and pmr spectra were measured as described elsewhere.<sup>13</sup>

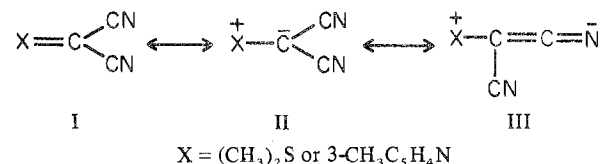
Molecular weights were determined in chloroform at 25 or 37° using a Mechrolab vapor pressure osmometer. The molecular weights of the ylide complexes are also listed in Table I.

## Results and Discussion

The ylides used here are represented by the canonical structures I–III. The  $\nu(\text{CN})$  bands of free ylides in the solid-state spectrum appear around 2190 and 2155 cm<sup>-1</sup>, as

Table II. Ir Data of the Ylide Complexes (cm<sup>-1</sup>)

Complex	$\nu(\text{CN})$		$\nu(\text{Pd-Cl})$ Nujol mull
	Nujol mull	Dichloro- methane	
Scy	2188, 2155	2188, 2161	
PdCl <sub>2</sub> (Scy) <sub>2</sub>	2224, 2211, 2188, 2157		344
PdCl <sub>2</sub> (PPh <sub>3</sub> )(Scy)	2224, 2180	2211, 2182, 2164	356
PdCl <sub>2</sub> (PPh <sub>2</sub> Me)(Scy)	2214, 2176	2213, 2180, 2165	361
Pd <sub>2</sub> Cl <sub>4</sub> (PPhMe <sub>2</sub> ) <sub>2</sub> (Scy)	2236, 2194	2208, 2178, 2164	359
PdCl <sub>2</sub> (AsPh <sub>3</sub> )(Scy)	2221, 2178	2215, 2180, 2164	362
Ncy	2191, 2160, 2136	2184, 2156, 2142	
Pd <sub>2</sub> Cl <sub>4</sub> (Ncy) <sub>2</sub>	2245, 2205, 2181		362
PdCl <sub>2</sub> (PPh <sub>3</sub> )(Ncy)	2210, 2184, 2162	2213, 2188, 2163, 2142	360
PdCl <sub>2</sub> (PPh <sub>2</sub> Me)(Ncy)	2207, 2177, 2156	2209, 2184, 2159	345
PdCl <sub>2</sub> (PPhMe <sub>2</sub> )(Ncy)	2204, 2172, 2153	2204, 2179, 2175, 2154	362



shown in Table II, which indicates a significant contribution of III,<sup>14</sup> in which lone-pair electrons of the ylide delocalize over the two cyano groups. Scy and Ncy have two coordination sites to metal halides; the coordination through the ylide carbon would lead to a high-frequency shift of  $\nu(\text{CN})$  due to an increasing contribution of II and that through a nitrile group would usually cause a high-frequency shift of  $\nu(\text{CN})$  as was shown in some nitrile complexes.<sup>16–19</sup> In fact,  $\nu(\text{CN})$  frequencies of the complexes prepared are higher than those of the original ylides as found in Table II. Therefore, the coordination site toward the palladium is not revealed from the shifts of  $\nu(\text{CN})$  frequency.

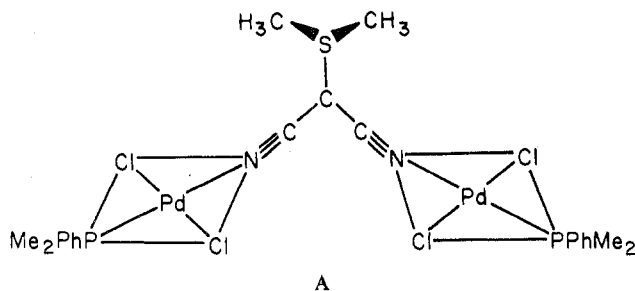
**The Sulfur Ylide Complexes.** It is to be noted that there is a close similarity in the structure between Scy<sup>20,21</sup> and tricyanomethanide anion (TCM);<sup>22,23</sup> both Scy and TCM have a trigonal-planar configuration around the central carbon atom. Mean bond lengths of the C–C (1.40 Å) and C–N (1.16 Å) bonds in Scy are essentially identical with those (1.40 and 1.15 Å) in TCM, respectively. The molecular orbital calculations on dicyanomethylene anion<sup>24</sup> and TCM<sup>25</sup> have indicated that a significant electron charge is placed on the nitrile nitrogen atoms. Furthermore, various first-row transition metal complexes of TCM are known to have a polymeric octahedral

**Table III.** Pmr Data of the Ylide Complexes in Dichloromethane at 23°

Complex	Chem shifts, $\delta$ Scy or Ncy CH <sub>3</sub>
Scy	2.76
PdCl <sub>2</sub> (Scy) <sub>2</sub> <sup>a</sup>	3.01, 2.72
PdCl <sub>2</sub> (PPh <sub>3</sub> )(Scy)	2.81
PdCl <sub>2</sub> (PPh <sub>2</sub> Me)(Scy)	2.84
Pd <sub>2</sub> Cl <sub>4</sub> (PPhMe <sub>2</sub> ) <sub>2</sub> (Scy)	2.85
PdCl <sub>2</sub> (AsPh <sub>3</sub> )(Scy)	2.85
Ncy	2.40
PdCl <sub>2</sub> (PPh <sub>3</sub> )(Ncy)	2.40
PdCl <sub>2</sub> (PPh <sub>2</sub> Me)(Ncy)	2.42
PdCl <sub>2</sub> (PPhMe <sub>2</sub> )(Ncy)	2.43

<sup>a</sup> In acetonitrile-*d*<sub>3</sub>.

configuration, in which each nitrogen atom of TCM is attached to a different metal ion.<sup>23,25,26</sup> In view of these facts and the elemental analysis, a Scy-bridged dimer configuration, A, may



be suggested for the Pd<sub>2</sub>Cl<sub>4</sub>(PPhMe<sub>2</sub>)<sub>2</sub>(Scy) complex. This configuration is in accordance with (i) the ir spectrum of the complex showing only one  $\nu(\text{Pd}-\text{Cl})$  band at 359 cm<sup>-1</sup> in the solid state (Table II) and (ii) the reaction of this compound with 2 molar equiv of *p*-toluidine in dichloromethane yielding the original sulfur ylide and *trans*-PdCl<sub>2</sub>(PPhMe<sub>2</sub>)(*p*-toluidine). That this compound in the solid state exhibits the highest  $\nu(\text{CN})$  frequencies among the Scy complexes obtained (Table II) also confirms the dinuclear configuration.

Molecular weight (Table I) and electrical conductivity<sup>27</sup> measurements indicate that Pd<sub>2</sub>Cl<sub>4</sub>(PPhMe<sub>2</sub>)<sub>2</sub>(Scy) partly dissociates into neutral species in solution. No isolation of the mononuclear complex with PPhMe<sub>2</sub> has, however, been successful even when 4 molar equiv of Scy was allowed to react with bis(dimethylphenylphosphine)dichloro- $\mu, \mu'$ -dichloro-palladium(II) in 1,2-dichloroethane at refluxing temperature.

The ir spectra of PdCl<sub>2</sub>L(Scy) (L = PPh<sub>3</sub>, PPh<sub>2</sub>Me, AsPh<sub>3</sub>) show only one  $\nu(\text{Pd}-\text{Cl})$  band around 360 cm<sup>-1</sup> in the solid state (Table II), suggesting that they are in a *trans* configuration around the palladium atom. In view of the fact that the frequencies of both  $\nu(\text{CN})$  and  $\nu(\text{Pd}-\text{Cl})$  are close to those of Pd<sub>2</sub>Cl<sub>4</sub>(PPhMe<sub>2</sub>)<sub>2</sub>(Scy), these mononuclear complexes would involve the coordination through one nitrile group of Scy to the palladium atom.

The isolation of the Pd(II) complex with two molecules, PdCl<sub>2</sub>(Scy)<sub>2</sub>, was established by elemental analysis. This compound is practically insoluble in less polar organic solvents, while a little soluble in more polar ones, such as acetonitrile. The pmr spectrum of a saturated solution in acetonitrile-*d*<sub>3</sub> shows two Scy CH<sub>3</sub> signals at  $\delta$  3.01 and 2.72 (Table III) with an integrated intensity ratio of 1:2. The ratio did not change down to -45°. The latter peak is assigned to the methyl protons of free Scy, which may be originally nitrogen bonded, because of its identical shift with Scy in acetonitrile. The former chemical shift is lower by about 0.15  $\delta$  unit than those of other Scy complexes, although solvents used are different (Table III).

The analogy between the oxygen atom and the dicyanomethylene group<sup>28-30</sup> makes the Scy ligand analogous to dimethyl sulfoxide (DMSO). The PdCl<sub>2</sub>(DMSO)<sub>2</sub> complex

is known to involve the sulfur-bonded ligand and exhibits a strong  $\nu(\text{Pd}-\text{S})$  band at 415 cm<sup>-1</sup>.<sup>31</sup> The ir spectrum of PdCl<sub>2</sub>(Scy)<sub>2</sub> shows a strong band at 378 cm<sup>-1</sup>, while no corresponding absorption occurs in other Scy complexes. The 378-cm<sup>-1</sup> band may therefore be assigned as the Pd-S vibration. Thus, the  $\delta$  3.01 signal in the pmr spectrum is attributed to the methyl protons of sulfur-bonded Scy. The occurrence of four  $\nu(\text{CN})$  bands in this complex also supports two kinds of Scy with different coordination atoms (nitrogen and sulfur) in the solid state, although there appears only one  $\nu(\text{Pd}-\text{Cl})$  band.

**The Nitrogen Ylide Complexes.** PdCl<sub>2</sub>L(Ncy) (L = PPh<sub>3</sub>, PPh<sub>2</sub>Me, PPhMe<sub>2</sub>) in the solid state shows only one  $\nu(\text{Pd}-\text{Cl})$  band, suggesting a *trans* configuration for these complexes. There is an analogy in the structure among TCM, Scy, and pyridinium dicyanomethylide.<sup>22,32</sup> This leads us to the conclusion that Ncy coordinates to the palladium atom through one nitrile group in these complexes. Molecular weight determinations confirm that all the Ncy complexes partly dissociate in solution. The pmr spectrum of PdCl<sub>2</sub>(PPh<sub>3</sub>)(Ncy) at room temperature gives one methyl signal of Ncy at  $\delta$  2.40, and at -28° one more signal appears at  $\delta$  2.48, which suggests the rate of dissociative exchange of Ncy is depressed at low temperature. In PdCl<sub>2</sub>(PPh<sub>2</sub>Me)(Ncy) and PdCl<sub>2</sub>(PPhMe<sub>2</sub>)(Ncy), such separated signals have not been observed at low temperature for the proximity in chemical shift between the coordinating and free Ncy.

There are two possible structures in the dinuclear complex of Pd<sub>2</sub>Cl<sub>4</sub>(Ncy)<sub>2</sub>; one is a chloride-bridged configuration, and the other a Ncy-bridged one analogous to Pd<sub>2</sub>Cl<sub>4</sub>(PPhMe<sub>2</sub>)<sub>2</sub>(Scy). In the ir spectrum down to 200 cm<sup>-1</sup>, only one  $\nu(\text{Pd}-\text{Cl})$  band is observed at 362 cm<sup>-1</sup>, which is assigned to the palladium-terminal chlorine stretching vibration. This result seems to indicate that the complex is a chloride-bridged dimer, though no palladium-bridged chlorine vibration has been found. The highest  $\nu(\text{CN})$  frequencies of this compound among the Ncy complexes obtained may be due to the fact that the Ncy is located *trans* to the bridged chloride. The pmr spectrum was not measured because of its low solubility in common organic solvents.

### Conclusion

That both Scy and Ncy complexes involve the palladium-nitrogen or -sulfur bond is a striking contrast to the case of methylphenylsulfonium *p*-chlorophenacylide, CH<sub>3</sub>-(C<sub>6</sub>H<sub>5</sub>)SCHC(O)C<sub>6</sub>H<sub>4</sub>Cl-*p*, which coordinates to Pd(II) and Pt(II) through the ylide carbon, as previously reported.<sup>13</sup> This is attributed to a reduction of the net charge on the ylide carbon in Scy and Ncy owing to a higher electronegativity of the cyano group than the carbonyl one. The present results clearly indicate that Scy and Ncy do not show the so-called ylide character in spite of having formal ylide structures.

Ncy seems to be a poorer donor than Scy in that the complexes with Ncy dissociate to a greater extent than the Scy complexes and that Ncy is less reactive than Scy. Indeed, Ncy does not react with bis(methyldiphenylphosphine)dichloro- $\mu, \mu'$ -dichloro-palladium(II) in dichloromethane, but Scy does. This may be due to the difference in geometry between Ncy and Scy; the latter has a planar-trigonal configuration around the central carbon atom. On the other hand, pyridinium dicyanomethylide is nonplanar around the ylide carbon, which causes a decrease of the negative charge on the nitrile groups<sup>32</sup> and hence a small affinity of Ncy toward Pd(II) ion. The weaker nitrogen-palladium bond in the Ncy complexes is also shown by the smaller  $\nu(\text{CN})$  shifts in Ncy than in Scy upon complex formation.

**Registry No.** PdCl<sub>2</sub>(Scy)<sub>2</sub>, 53092-84-5; PdCl<sub>2</sub>(PPh<sub>3</sub>)(Scy), 53111-29-8; PdCl<sub>2</sub>(PPh<sub>2</sub>Me)(Scy), 53111-30-1; Pd<sub>2</sub>Cl<sub>4</sub>(PPhMe<sub>2</sub>)<sub>2</sub>(Scy), 53111-32-3; PdCl<sub>2</sub>(AsPh<sub>3</sub>)(Scy), 53111-31-2;

$\text{Pd}_2\text{Cl}_4(\text{Ncy})_2$ , 53111-33-4;  $\text{PdCl}_2(\text{PPh}_3)(\text{Ncy})$ , 53111-34-5;  $\text{PdCl}_2(\text{PPh}_2\text{Me})(\text{Ncy})$ , 53111-35-6;  $\text{PdCl}_2(\text{PPhMe}_2)(\text{Ncy})$ , 53111-36-7; Scy, 5362-78-7; Ncy, 3189-56-8; bis(dimethylphenylphosphine)dichloro- $\mu, \mu'$ -dichloropalladium(II), 15699-80-6; bis(triphenylphosphine)dichloro- $\mu, \mu'$ -dichloropalladium(II), 15134-30-2; bis(methyldiphenylphosphine)dichloro- $\mu, \mu'$ -dichloropalladium(II), 29887-90-9; bis(benzonitrile)dichloropalladium(II), 14220-64-5.

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## Investigation of the Second Coordination Sphere in Inorganic Complexes by Dynamic Nuclear Polarization (Dnp). Complexes with Electron Spin Residing on the Metal Atom<sup>1</sup>

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The solvation of inert, low-spin Cr(I) complexes by nmr-active species in the second coordination sphere has been investigated by dynamic nuclear polarization (dnp), an nmr-esr double-resonance technique. At 75-G magnetic field, dipolar (through-space) and scalar (Fermi-contact) interaction between a nuclear spin and an electron spin on different molecules can be distinguished. Only dipolar coupling was observed for  $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$  and the nuclear test probes octafluoronaphthalene (OFN), trimethyl phosphite,  $\text{Li}^+$ , and  $\text{BF}_4^-$ . There is little unpaired spin density at the periphery of the nitrosyl complex. The order of observed solvation interaction is  $\text{BF}_4^- < \text{H}_2\text{O} < \text{Li}^+$ , demonstrating electrostatic effects. With  $\text{Cr}(\text{bipy})_3^+$ , moderate scalar coupling is observed for OFN and the phosphite, indicating the presence of unpaired spin density in the plane of the bipyridyl ring, at the rim of the complex. With  $\text{Cr}(\text{C}_6\text{H}_6)_2^+$  serving as radical probe, strong scalar coupling by transient bonding interaction is observed for trimethyl phosphite and for  $\text{BF}_4^-$ . The absence of scalar coupling with OFN suggests a lack of unpaired spin density above the planes of the  $\pi$ -benzene rings. The data are consistent with penetration of small ligands into the space between the benzene rings and transient bond formation directly with the metal. The general applicability of dnp to the study of second coordination sphere molecular interactions having correlation times shorter than  $10^{-8}$  sec is discussed.

### Introduction

A metal complex in solution interacts with surrounding solvent molecules, counterions, or other dissolved species. The importance of this second coordination sphere (SCS) in ligand-exchange reactions, and to catalysis in general, is beginning to be realized.<sup>2</sup> Nmr is one of the few techniques that can yield information at the molecular level about interactions occurring at the outer fringes of a complex.<sup>2,3</sup> Dipolar broadening of nmr lines sometimes allows the detection of preferential orientation of molecules near the surface of a paramagnetic complex.<sup>4,5</sup> Distances of closest approach and solvation geometries can sometimes be deduced from dipolar

(pseudocontact) chemical shifts of solvent molecules positioned in the SCS of transition metal complexes exhibiting strong  $g$ -tensor anisotropy.<sup>2,6</sup>

The present work examines the applicability of dynamic nuclear polarization (dnp), a double-resonance nmr-esr technique, as a tool for studying SCS interactions of paramagnetic ions in solution. Dnp measures the weak coupling between nuclear spins on one molecule and an electron spin on another molecule during encounters of the two species in solution. As the technique is only responsive to fast molecular interactions (correlation times shorter than  $10^{-8}$  sec), it is especially suited for investigations of diffusion-controlled