Table I. Infrared Frequencies (cm^{-1}) in the Carbonyl Region for Nickel Carbonyl Derivatives

anion[a]	ν_{CO}[b]
$W_2Ni_3(CO)_{16}^{2-}$	2036 (w), 1998 (s), 1930 (mw), 1896 (s), 1835 (m), 1791 (w)
$CrNi_6(CO)_{17}^{2-}$[c]	2060 (w), 2008 (vs), 1971 (w),[d] 1911 (m), 1894 (s), 1940 (m), 1810 (s), 1780 (s), 1867 (s), 1831 (m)
$MoNi_6(CO)_{17}^{2-}$[c]	2059 (w), 2005 (vs), 1969 (m),[d] 1940 (m), 1910 (mw), 1892 (s), 1861 (s), 1831 (m), 1801 (s), 1771 (s)
$WNi_6(CO)_{17}^{2-}$	2056 (w), 2000 (vs), 1954 (sh), 1933 (m), 1903 (m), 1887 (s), 1854 (s), 1822 (m), 1794 (s), 1769 (s)

[a] PPN$^+$ salts. [b] Nujol mulls. [c] Unable to be isolated. [d] Unreacted $Ni_6(CO)_{12}^{2-}$.

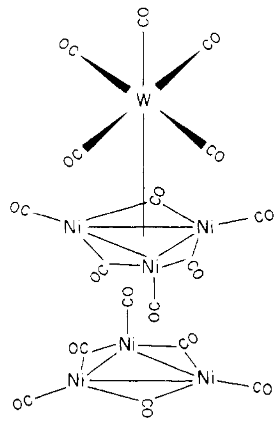

Figure 1. Proposed structure for the $WNi_6(CO)_{17}^{2-}$ ion.

and 197.5 (3) ppm (the numbers in parentheses are the relative peak areas). They are assigned to the bridging carbonyls on nickel, the axial carbonyl on tungsten, the equatorial carbonyl on tungsten, and the terminal carbonyls on nickel, respectively. A suggested structure for the $WNi_6(CO)_{17}^{2-}$ ion is shown in Figure 1.

Although several attempts were made to add two $W(CO)_5$ units to the $Ni_6(CO)_{12}^{2-}$ anion, they were not successful. Using a large excess of $W(CO)_5$·THF led only to the monocapped species while extended reaction times at reflux resulted in the formation of the known $W_2Ni_3(CO)_{16}^{2-}$ cluster. Simultaneous photolysis of $W(CO)_6$ and $Ni_6(CO)_{12}^{2-}$ also produced $W_2Ni_3(CO)_{16}^{2-}$ in moderate yields. It is possible that the $WNi_6(CO)_{17}^{2-}$ ion is an intermediate in the reaction of $W_2CO_{10}^{2-}$ with $Ni(CO)_4$ since upon either refluxing, photolysis, or reaction with excess $W(CO)_6$ it is converted to the $W_2Ni_3(CO)_{16}^{2-}$ cluster. Similar behavior was observed for the other two nickel clusters. Thus, $Ni_5(CO)_{12}^{2-}$ and $Ni_9(CO)_{18}^{2-}$ were converted to $W_2Ni_3(CO)_{16}^{2-}$ upon refluxing with $W(CO)_6$ in THF. That these systems are quite labile and undoubtedly involve a number of equilibria was further demonstrated by allowing the $W_2Ni_3(CO)_{16}^{2-}$ ion to react with excess $Ni(CO)_4$. Either $Ni_6(CO)_{12}^{2-}$ or $Ni_9(CO)_{18}^{2-}$ could be isolated depending on reaction times and the amount of $Ni(CO)_4$ used. In fact, reaction of $Ni(CO)_4$ with the $W_2(CO)_{10}^{2-}$ ion produces the nickel clusters if a very large excess of $Ni(CO)_4$ is employed. These reactions are summarized in Figure 2. Included are some reactions of the clusters $W_2Ni_3(CO)_{16}^{2-}$, $Ni_6(CO)_{12}^{2-}$, $Ni_5(CO)_{12}^{2-}$, and $Ni_9(CO)_{18}^{2-}$ which have previously been reported. The transformations represented in Figure 2 obviously do not represent balanced equations since only the most accessible product(s) were isolated.

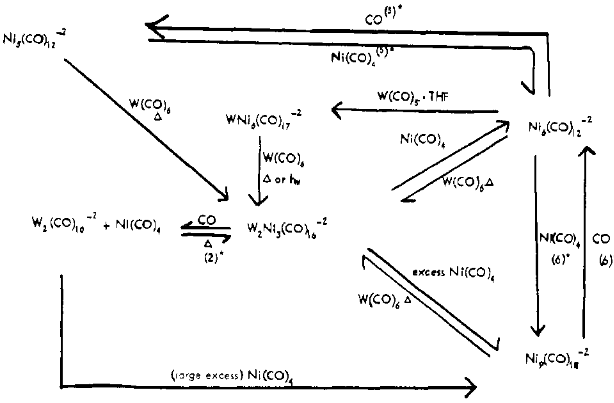

Figure 2. Reaction equilibria in anionic nickel and tungsten carbonylate systems. Asterisks signify known reactions; numbers refer to references.

The question of characterization of individual clusters in these complex systems is very difficult. Infrared spectroscopy is useful only for identifying known compounds in reaction mixtures (i.e., in this case, $Ni_6(CO)_{12}^{2-}$, $Ni_5(CO)_{12}^{2-}$, $Ni_9(CO)_{18}^{2-}$, and $W_2Ni_3(CO)_{16}^{2-}$). Inferences regarding structure and/or symmetry of new cluster systems are dubious since it is not possible to rely on the group character tables and the lack of accidental degeneracies. The infrared spectra of the new clusters in the CO region are given in Table I. Thus, in the final analysis, X-ray structural determination remains the ultimate tool for characterization.

Acknowledgment. This work was, in part, supported by an Alfred P. Sloan Fellowship.

Registry No. $(PPN)_2WNi_6(CO)_{17}$, 79466-70-9; $CrNi_6(CO)_{17}^{2-}$, 79391-49-4; $MoNi_6(CO)_{17}^{2-}$, 79391-50-7; $(PPN)_2Ni_6(CO)_{12}$, 60464-20-2; $(PPN)_2Ni_9(CO)_{18}$, 60512-59-6; $(PPN)_2W_2Ni_3(CO)_{16}$, 11059-51-1; $(PPN)BH_4$, 65013-26-5; $(PPN)_2W_2(CO)_{10}$, 52580-40-2; $Ni(CO)_4$, 13463-39-3; $W(CO)_6$, 14040-11-0; (PPN)Cl, 21050-13-5.

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Formation of Bridged Group 4B Metal to Group 8 Metal Polymers

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It is well-known that metal cyanide complexes can act as Lewis bases through the nitrogen atom to form C–N bridges to compounds with Lewis acid centers.[1,2] Indeed, Manzer and Parshall[3] used this property to investigate the order of Lewis acidity of AlR_3 and BR_3 compounds through their reactions with $HPtL_2CN$ (L is PPh_3). They also showed that $HPtL_2CN$ reacts with metal-centered Lewis acids such as $NiCl_2$ to give monomeric cyanide-bridged products. From studies on Prussian blue and its analogues,[4] it is also clear that three-dimensional networks bound by M–C–N–M′ units can form upon crystallization of polyfunctional metal cyanide ions with other transition-metal ions.

These facts suggest that it should be possible to synthesize quasilinear cyanide-bridged metal-containing polymers through the interaction of bifunctional Lewis acid metal atom centers and metal cyanide species which have at least two cyanides and to incorporate in the material a functionally basic metal center. However, Rupp and Shriver[5] found that when Fe-

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(2) J. S. Kristoff and D. F. Shriver, *Inorg. Chem.*, **12**, 1788 (1973).
(3) L. E. Manzer and G. W. Parshall, *Inorg. Chem.*, **15**, 3114 (1976).
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$(phen)_2(CN)_2$ is reacted with MF_4 (M = Si, Ge, Sn) species, which can act as bifunctional Lewis acids by increasing their coordination number from 4 to 6 concomitant with the reaction, the products are simply substituted or cyclic species rather than polymers. For example, a ring containing two Fe, two Si atoms, and four CN bridges was proposed as the central unit in the product $(Fe(phen(Ph)_2)_2(CN)_2SiF_4)_2$.

We concluded that such polymers could be formed via nucleophilic substitution of strongly basic cyanometallate ions for weakly basic ligands at the strongly acidic sites on Zr or Hf atoms under conditions in which the reactants would not oxidize or reduce, change in coordination number, or undergo competing solvolysis.

The group 4B dihalometallocenes $(\eta^5\text{-}C_5H_5)_2MX_2$ (X = Cl, Br, I; M = Zr, Hf) fulfill the requirements for the bifunctional Lewis acid, since the halides can be exchanged by metastasis, and the group 4B atom is strongly acidic, not easily reduced, not expected to add oxidatively to metal cyanide complexes, and expected to retain four-coordination under attainable experimental conditions. Moreover, they are known to react with bifunctional organic carboxylic acids to form polymeric species.[6]

The square-planar tetracyanometallate anions of Pt(II) and Pd(II), $M'(CN)_4^{2-}$, fulfill the requirements for the bifunctional Lewis base since they are stable in the absence of species which can either add to them oxidatively or oxidize them to M(IV) in the presence of basic solvents. Although it is recognized that they could act as Lewis bases through the M′ atom, as in extended metal-chain interactions,[7] and that bonds to the bis(cyclopentadienyl)zirconium moiety have been formed with basic metal centers,[8] reaction of $M(CN)_4^{2-}$ ions through the CN groups with $(\eta^5\text{-}C_5H_5)_2ZrI_2$ and $(\eta^5\text{-}C_5H_5)_2HfI_2$ appeared to present routes to quasilinear group 4B and 8 metal-containing polymers. In them, the M′(II) center would remain weakly basic and be a site for oxidative addition reactions.

We report that reactions of $(\eta^5\text{-}C_5H_5)_2ZrI_2$ and $(\eta^5\text{-}C_5H_5)_2HfI_2$ with $Pt(CN)_4^{2-}$ and with $Pd(CN)_4^{2-}$ in solution lead to polymeric amorphous solids having elemental analyses corresponding to $((\eta^5\text{-}C_5H_5)_2MM'(CN)_4)_n$ (where M = Zr, Hf; M′ = Pt, Pd).

Experimental Section

All procedures were carried out under Ar or in vacuo with dried, deaerated solvents, acetonitrile, CH_3CN, or dichloromethane, CH_2Cl_2. The $(\eta^5\text{-}C_5H_5)_2MI_2$ materials (M = Zr, Hf) were synthesized by reaction of stoichiometric amounts of $(\eta^5\text{-}C_5H_5)_2MCl_2$ (M = Zr, Hf) (Alfa Inorganics) with BI_3 (Alfa Inorganics) in CH_2Cl_2 under Ar (also affording BCl_3 which was removed under vacuum) and purified by recrystallization from CH_2Cl_2.[10] The $[(n\text{-}C_4H_9)_4N]_2M'(CN)_4$ (M′ = Pt, Pd) salts were prepared by cation exchange in acetonitrile between $(n\text{-}C_4H_9)_4NCl$ and $K_2M'(CN)_4$, synthesized by the method of Abys et al.[11] The products were dried in vacuo at 70 °C.

$(\eta^5\text{-}C_5H_5)_2ZrPt(CN)_4$ was prepared by the reaction of $(\eta^5\text{-}C_5H_5)_2ZrI_2$ and $[(n\text{-}C_4H_9)_4N]_2Pt(CN)_4$, employed to yield a soluble side product, in acetonitrile. In a typical reaction, 1.27 g of $(\eta^5\text{-}C_5H_5)_2ZrI_2$ was reacted with 2.11 g of $[(n\text{-}C_4H_9)_4N]_2Pt(CN)_4$ in 0.3 L of CH_3CN for 4 h at 30 °C and yielded a yellow precipitate and a solution of $(n\text{-}C_4H_9)_4NI$. The precipitate was washed with CH_3CN and freed of solvent in vacuo at 80 °C for 24 h to afford 1.36 g of the product (98% yield). The elemental analysis (Galbraith Laboratories) gives (found) $Zr_{1.05}Pt_{0.95}C_{14.1}N_{4.0}H_{11.1}$, in good agreement with that calculated for $[(\eta^5\text{-}C_5H_5)_2ZrNCPt(CN)_2CN]_n$ of $Zr_1Pt_1C_{14}N_4H_{10}$. The compound is diamagnetic ($\chi = -0.085 \times 10^{-6}$ cgs at 10.4 G, -0.1 ± 0.05 in the 5–11-kG range), is X-ray amorphous,[12] has principal infrared absorptions at 2165 (s), 2144 (s), 1128 (m), 1070 (m), 1025 (s), 1013 (s), 822 (vs), 615 (w), 520 (w), 570 (w), 485 (s), and 427 (w), and decomposes without melting above 350 °C.

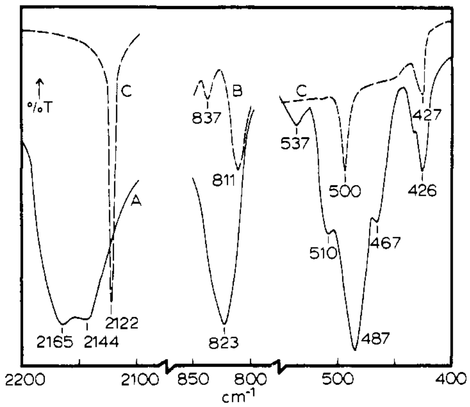

Figure 1. Infrared spectral features of $[(\eta^5\text{-}C_5H_5)_2ZrPt(CN)_4]_n$ (A), and of the related $((C_4H_9)_4N)_2Pt(CN)_4$ (C) and $(\eta^5\text{-}C_5H_5)_2ZrI_2$ (B).

$(\eta^5\text{-}C_5H_5)_2ZrPd(CN)_4$ was prepared analogously, in 96% yield. The elemental analysis gave is $Zr_{1.0}Pd_{1.0}C_{14.2}N_{4.04}H_{11.0}$, in good agreement with $Zr_{1.0}Pd_{1.0}C_{14.0}N_{4.0}H_{10.0}$. The compound is diamagnetic, is X-ray amorphous, has principal infrared absorptions at 2170 (s), 2150 (sh), 1128 (m), 1069 (m), 1013 (s), 820 (vs), 606 (m), 515 (m), and 438 (s), and decomposes without melting above 375 °C.

$(\eta^5\text{-}C_5H_5)_2HfPt(CN)_4$ and $(\eta^5\text{-}C_5H_5)_2HfPd(CN)_4$ were synthesized in the same manner, giving yellow products in 95–98% yield with the elemental analyses $Hf_{1.0}Pt_{1.08}C_{12}N_{3.8}H_{9.8}$ and $Hf_{1.1}Pd_{1.0}C_{14.3}N_{3.8}H_{10.5}$. They too are X-ray amorphous, diamagnetic, and insoluble in polar solvents. The principal infrared bands of $(\eta^5\text{-}C_5H_5)_2HfPt(CN)_4$ were observed at 2174 (s), 2150 (s), 1128 (m), 1069 (m), 1025 (s), 1013 (s), 920 (w), 823 (vs), 605 (w), 540 (w), 512 (m), 489 (s), and 430 (w), while those of $(\eta^5\text{-}C_5H_5)_2HfPd(CN)_4$ were found at 2174 (s), 2150 (sh), 1130 (m), 1070 (m), 1025 (s), 1015 (s), 827 (vs), 605 (w), 516 (w), and 447 (s). They decompose without melting above 280 and 310 °C, respectively.

The infrared spectra were measured on Nujol mulls on a Digilab FT-15B interferometer, and the Raman spectra were measured on a Jarrell-Ash 25-300 spectrometer employing the 488.0-nm radiation of an Ar^+ laser and the 632.8-nm radiation of a He–Ne laser. The X-ray measurements were made with a Debye–Scherrer camera with Ni-filtered Cu Kα radiation. Magnetic susceptibilities were measured at room temperature on a Faraday electrobalance, and all four compounds exhibited diamagnetic moments of −0.1 ± 0.05 in the 5–11-kG range.

Results and Discussion

The principal features of the infrared spectra of these four products of the form $((\eta^5\text{-}C_5H_5)_2MM'(CN)_4)_n$ are similar and consistent with the assignment of the polymeric structure shown below. They are illustrated by the spectrum of $((\eta^5\text{-}C_5H_5)_2ZrPt(CN)_4)_n$ (A) shown in Figure 1 with key bands of the starting materials. The regions of interest contain the ν(CN), $\delta(C_5H_5)$, ν(M′–CN), and ν(N–M) vibrations. The single ν(CN) band of $((C_4H_9)_4N)_2Pt(CN)_4$ at 2122 cm⁻¹ is replaced in A by two bands at 2165 and 2144 cm⁻¹, as expected for D_{2h} local symmetry. The 2165-cm⁻¹ band, broadened and shifted by nearly +45 cm⁻¹ relative to $Pt(CN)_4^{2-}$, is assigned to a bridging cyanide vibration (B_{3u} in local D_{2h}). The

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(8) P. Renant, G. Tainturier, and B. Gantheron, *J. Organomet. Chem.*, **150**, C9 (1978).

(9) The reaction of $[(\eta^5\text{-}C_5H_5)_2ZrPt(CN)_4]_n$ with $Br_2(g)$ under vacuum conditions proceeds with formation of a tan product whose spectrum is consistent with oxidative addition of Br_2 to yield $[(\eta^5\text{-}C_5H_5)_2ZrPt(CN)_4Br_2]_n$. However, reaction with Br_2 in solution yields different products, apparently also involving bromination of the cyclopentadiene ligands. These and other reactions are under investigation.

(10) P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding, and R. M. Srivastava, *J. Chem. Soc. A*, 2106 (1969).

(11) J. A. Abys, N. P. Enright, H. M. Gerdes, T. L. Hall, and J. M. Williams, *Inorg. Synth.*, **19**, 1, and references therein.

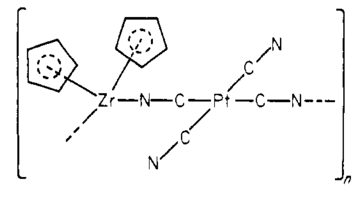
(12) There are very weak, diffuse intensity gradients on the films which may be due to scattering from spacings of high Z atomic centers, i.e., Zr and Pt in the $[(\eta^5\text{-}C_5H_5)_2ZrPt(CN)_4]_n$ case. With the assumption that this is their origin, the distances may be estimated by standard methods from the centers of the diffuse rings as 4.86, 7.80, and 10.3 nm and compared to the estimated (calculated) distances for the proposed structure of Zr–Pt 4.71 nm, Pt–Pt 7.63 nm, and Zr–Zr 9.42 nm.

2144-cm^{-1} band is assigned to a terminal C–N stretch (B_{2u}) whose shift to higher frequency relative to $Pt(CN)_4^{2-}$ is attributed to a slight decrease in the π back-bonding to the CN ligand from the Pt atom. If the bridging CN ligands were cis, the local symmetry about Pt would be C_{2v} and four ν(CN) modes would be expected in the infrared and they would be coincident with the Raman bands, neither of which is true for A. Similarly, overall D_{2h} symmetry for a cyclic dimer would lead to eight IR-active ν(CN) (presumably four sets of double accidentally degenerate ones), and this is not observed. The shift in δ(C–H) from 811 to 823 cm^{-1}, together with other cyclopentadiene features, shows retention of π bonding between the cyclopentadiene and Zr and the increase in positive charge density on Zr. The 350–650-cm^{-1} region contains six bands including the ν(Pt–C) and ν(Zr–N) modes expected for the polymeric structure proposed below. In particular, the Zr–N stretch is observed at 510 cm^{-1}. The ν(Zr–I) bands of $(\eta^5\text{-}C_5H_5)_2ZrI_2$ are absent from the spectrum of A.

The Raman spectrum of $[(\eta^5\text{-}C_5H_5)_2ZrPt(CN)_4]_n$ contains the features expected for a cyanide-bridged species containing both the zirconocene and terminal cyanide-containing platinum moieties. There are no Raman bands of any of the homologs that clearly would be assigned to metal–metal bond stretches.

X-ray diffraction experiments on the product powders showed diffuse scattering characteristic of amorphous materials. Magnetic susceptibility measurements showed them to be diamagnetic. Due to their insolubility in common solvents, and their involatility, their molecular weights could not be determined.

On the basis of the observed properties, we propose the structure of A, in which the tetrahedral coordination about Zr and the square-planar coordination about Pt are retained. Analogous structures are proposed for $[(\eta^5\text{-}C_5H_5)_2ZrPd(CN)_4]_n$, $[(\eta^5\text{-}C_5H_5)_2HfPt(CN)_4]_n$, and $[(\eta^5\text{-}C_5H_5)_2HfPd(CN)_4]_n$.



A

The compounds synthesized possess features which present interesting chemical possibilities. For example, since the Pt (or Pd) is in the II state formally, it is a site for oxidative addition,[9] and it is feasible that ligands added in this way could be substituted for by a metal-containing nucleophile to give branched, and perhaps cross-linked, metal-containing polymers. Alternatively, such oxidative addition at M′ could weaken the CN–M interaction enough to permit weak nucleophiles, which normally could not compete effectively for M sites, to form compounds with the 4B metals. In addition, the presence of the two coordinatively and electronically unsaturated metals in these compounds may lend them catalytic activity, and this possibility is under investigation.

Acknowledgment. The support of the Materials Science Program of Brown University, sponsored by the National Science Foundation, is gratefully acknowledged. We are grateful to Ms. June Passaretti, Dr. Richard Collins, and Professor Aaron Wold of the Chemistry Department and the M.R.L. Materials Preparation Facility for assistance in obtaining the X-ray and magnetic data.

Registry No. $[(\eta^5\text{-}C_5H_5)_2ZrPt(CN)_4]_n$, 78891-74-4; $[(\eta^5\text{-}C_5H_5)_2ZrPd(CN)_4]_n$, 78891-72-2; $[(\eta^5\text{-}C_5H_5)_2HfPt(CN)_4]_n$, 78891-70-0; $[(\eta^5\text{-}C_5H_5)_2HfPd(CN)_4]_n$, 78891-68-6; $(\eta^5\text{-}C_5H_5)_2ZrI_2$, 1298-41-5; $(\eta^5\text{-}C_5H_5)_2HfI_2$, 37260-85-8; $[(n\text{-}C_4H_9)_4N]_2Pt(CN)_4$, 21518-40-1; $[(n\text{-}C_4H_9)_4N]_2Pd(CN)_4$, 21518-39-8.

Correspondence

Alterdentate Ligands

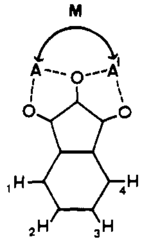
Sir:

In coordination chemistry, ligands have been classified according to various criteria. One obvious classification concerns the *denticity* of a ligand and, consequently, sequestring agents are called *unidentate*, *bidentate*, etc.[1] Another widely accepted designation is *ambidentate*,[2] which means that a ligand can coordinate through *different* ligand atoms as, e.g., nitrogen and sulfur in the thiocyanate NCS^- ion. Is the azide ion NNN^- ambidentate too?

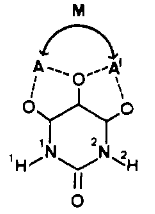
In the present paper we want to propose a designation for a class of ligands, which can form metal complexes that can undergo some well-defined modes of rearrangements.

We define as an *alterdentate ligand* a species which offers to a metal ion more than one *equivalent* coordination site. In an alterdentate ligand there is, principally, always a rearrangement possible in which the metal is transferred from one site to another one. This can be either an inter- or intramolecular process. The rearrangement reaction is kinetically controlled by the activation energy and entropy experienced by the metal on the reaction path. The free energy difference is zero by definition, if the coordination sites are equivalent.

Examples for such alterdentate ligands are found in the recently reported complexes of ninhydrine (I) or alloxan (II) radical anions.[3] In both cases, A and A′ are equivalent coordination sites and, consequently, $\Delta G° = 0$ for (1) and (2).



nin$^-$ (I)



all$^-$(II)

$$\mathrm{M(A)(nin^-)} \rightleftarrows \mathrm{M(A')(nin^-)} \tag{1}$$

$$\mathrm{M(A)(all^-)} \rightleftarrows \mathrm{M(A')(all^-)} \tag{2}$$

The exchange between A and A′ can be observed by ESR spectroscopy because the spin densities at the positions H(1) to (4) in nin$^-$ and (HN)(1)/(HN)(2) in all$^-$ are modulated

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(3) Schaller, D.; von Zelewsky, A. *J. Chem. Soc., Chem. Commun.* **1979**, 948.

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