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Synthesis and Structure of 1,2,3,4,5-Pentamethylcyclopentadienyl-1,4-Diphenyltetraazabutadiene Complexes of Rhodium and Iridium

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Monomeric rhodium and iridium-diaryltetraene complexes $Cp^*M(RNN=NNR)(Cp^*=1,2,3,4,5\text{-pentamethylcyclopentadienyl}; M=Rh, Ir; R=Ph, 4\text{-tolyl})$ have been synthesized from $[Cp^*MCl_2]_2 (M=Rh, Ir)$ and 2 equiv. of $[Li(THF)_2]_2 (RN_4R)$ in benzene. We have determined the crystal structure of $(\eta^5\text{-pentamethylcyclopentadienyl})diphenyltetraazabutadiene$ iridium by using graphite-monochromated $Mo\text{-}K\alpha$ radiation. The compound was crystallized in the monoclinic space group $P2_1/c$ with $a=13.781(3)$, $b=9.035(1)$, $c=17.699(3)$ Å, and $\beta=111.93(1)^\circ$. An X-ray crystal structure of complex **1** showed a short N(2)-N(3) distance (1.265 Å) consistent with the valence tautomer A with Ir(III) rather than Ir(I). All complexes are highly colored and decompose on irradiation at 254 nm. Electrochemical studies show that complex **1** displays a quasi-reversible reduction.

Introduction

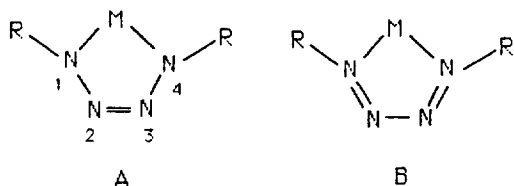
Since the discovery of $[Fe(R_2N_4)(CO)_3]$ in 1967¹, transition-metal tetraazadiene complexes have been reported, including derivatives of Ni, Co, Ir, Rh, and Pt by coupling reactions between an organic azide and a metal complex in a low oxidation state or tetrazenido dianion and transition-metal dihalide complex.²⁻⁹

Transition-metal tetraazadiene complexes have attracted interest because of their novel bonding mode and the possibility of dinitrogen extrusion. It has been suggested that resonance structures A and B contribute to the overall structure of tetraene complexes.^{10,11} The formal valence structure A or B in the complex was adopted by the extent the delocali-

zation of π -electron density in the metallacycles and the role of the metal d orbitals in bonding. Backbonding from the metal to the lowest ligand π -acceptor orbital would induce the bond length variation found in structure A. In particular, the structure A gives us a good model of nitrogen extrusion because of the weak bond strength of N(1)-N(2). The fact stimulates us to explore the preparation of the complexes of the type A by changing the ligand attached to the transition-metal. Herein we reported the syntheses of transition-metal tetraazadiene complexes by the reaction of Rh and Ir complexes with tetrazenido dianion.

Experimental Section

All manipulations of air-sensitive materials were carried out under an argon atmosphere with use of standard Schlenk or vacuum line technique or a Mebraun MB150 glovebox. ¹H-NMR spectra were recorded on a Bruker WM-250 spectrometer in $CDCl_3$. Chemical shifts are given in parts per million relative to TMS for ¹H-NMR spectra. IR spectra were obtained by using a Perkin-Elmer 1310 instrument. Mass spectra were measured on a high resolution VG70-VSEG



spectrometry. Cyclic voltammetry was carried out with a Potentiostat-Galvanostat Model 273 at a glassy-carbon electrode with an Ag/AgCl couple as a reference and *tetra-n*-butyl ammonium perchlorate (TBAP) as an electrolyte in CH₃CN. Elemental analyses were carried out at Basic Science Center. Reagent grade THF and benzene were distilled under argon from sodium-benzophenone ketyl. Pentane and hexane were distilled under Ar from sodium. [(η⁵-C₅Me₅)MCl₂]₂ (M=Rh, Ir)¹², PhN₃¹³, and [Li(THF)_x]₂[RNN=NNR] (R=C₆H₄-CH₂-C₆H₄)¹⁴ were prepared according to literature methods. MCl₃·xH₂O (M=Rh, Ir) were purchased from Strem Chemical Inc. 1,2,3,4,5-pentamethylcyclopentadiene, *n*-BuLi, and 1,5-cyclooctadiene were purchased from Aldrich.

Preparation of [Cp*Ir(1,4-N₄Ph₂)] (1). To a stirred benzene solution (25 ml) of [Cp*IrCl₂]₂ (0.52 g, 0.65 mmol; Cp*=1,2,3,4,5-pentamethylcyclopentadiene) was added [Li(THF)_x]₂[PhNN=NNPh] (0.29 g, 1.30 mmol) in benzene (25 ml) dropwise. The solution was stirred at room temperature for 24 h. The volume was reduced to ca. 10 ml and the solution was filtered off. The reddish-yellow crystals were obtained by layering pentane (30 ml) to the solution and leaving the solution in a refrigerator at 0°C. The yield was 27%. mp. 161°C. ¹H-NMR (C₆D₆): δ 7.39-7.17 (m, 10H, aromatic), 1.49 (s, 15H, C₅Me₅); IR (on KBr pellet; cm⁻¹) 3042 (w), 3024 (w), 2974 (w), 2882 (m), 1493 (m), 1362 (m), 1288 (m), 1261 (br), 1168 (w), 1158 (w), 1078 (w), 1062 (w), 1035 (br), 942 (w), 932 (w), 778 (w), 762 (s), 699 (s); mass spectrum, m/e (relative intensity) 538 (M⁺, 38), 510 (M⁺-N₂, 54), 419 (M⁺-PhN₃, 98). Anal. Calcd. for C₂₂H₂₅IrN₄: C, 49.16; H, 4.65. Found: C, 48.76; H, 4.49.

Preparation of [Cp*Rh(1,4-Ph₂N₄Ph)] (2). To a stirred benzene solution (25 ml) of [Cp*RhCl₂]₂ (0.75 g, 1.21 mmol) was added [Li(THF)_x]₂[PhNN=NNPh] (0.54 g, 2.42 mmol) in benzene (25 ml) dropwise. The solution was stirred at room temperature for 24 h. The volume was reduced to ca. 10 ml and the solution was filtered off. The reddish-brown crystals were obtained by layering pentane (30 ml) to the solution and leaving the solution in a refrigerator at 0°C. The yield was 32%. mp. 157°C. ¹H-NMR (CDCl₃): δ 7.44-7.26 (m, 10H, Ph), 1.53 (s, 15H, C₅Me₅); IR (on KBr pellet; cm⁻¹) 3042 (w), 2964 (w), 2958 (w), 2895 (w), 1754 (w, br), 1476 (m), 1442 (w), 1378 (br), 1273 (m), 1242 (m), 1152 (w), 1143 (w), 1132 (w), 1091 (w), 1072 (w), 1062 (w), 1032 (w), 998 (w), 932 (w), 905 (w), 762 (s), 742 (m), 698 (s); mass spectrum, m/e (relative intensity) 448 (M⁺, 68), 420 (M⁺-N₂, 52), 252 (M⁺-Ph₂N₃, 97). Anal. Calcd. for C₂₂H₂₅RhN₄: C, 58.96; H, 5.58. Found: C, 58.62; H, 5.47.

Preparation of [Cp*Rh(1,4-tolylN₄tolyl)] (3). The same procedure was taken as described in the preparation of **1**. The yield was 22%. mp. 165°C. ¹H-NMR (CDCl₃): δ 7.52-7.21 (m, 8H, aromatic), 1.42 (s, 15H, C₅Me₅), 1.18 (s, 6H, CH₃); IR (on KBr pellet; cm⁻¹) 3032 (w), 2978 (w), 2856 (m), 1478 (m), 1387 (m), 1372 (m), 1284 (m), 1258 (br), 1178 (w), 1164 (w), 1071 (m), 1062 (w), 1044 (br), 963 (w), 948 (w), 928 (w), 798 (w), 776 (w), 754 (s), 687 (s); mass spectrum, m/e (relative intensity) 476 (M⁺, 38), 448 (M⁺-N₂, 48). Anal. Calcd. for C₂₄H₂₉RhN₄: C, 60.54; H, 4.79. Found: C, 61.22; H, 4.87.

Preparation of [Cp*Ir(1,4-tolylN₄tolyl)] (4). The same procedure was taken as described in the preparation of **1**. The yield was 36%. mp. 170°C. ¹H-NMR (CDCl₃): δ

7.48-7.12 (m, 8H, aromatic), 1.39 (s, 15H, C₅Me₅), 1.22 (s, 6H, CH₃); IR (on KBr pellet; cm⁻¹) 3036 (w), 3024 (w), 2992 (m), 2948 (m), 2872 (m), 1472 (m), 1384 (m), 1370 (m), 1358 (m), 1287 (m), 1272 (m), 1252 (br), 1175 (w), 1160 (w), 1052 (w), 1040 (br), 958 (w), 942 (w), 922 (w), 789 (w), 772 (w), 748 (s), 682 (s); mass spectrum, m/e (relative intensity) 566 (M⁺, 44), 538 (M⁺-N₂, 56). Anal. Calcd. for C₂₄H₂₇IrN₄: C, 50.98; H, 5.12. Found: C, 51.36; H, 5.29.

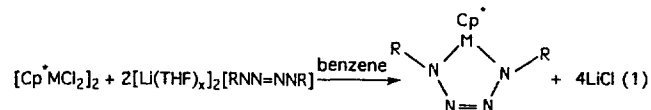
Crystal structure of 1. The crystal of **1** was grown from benzene/hexane at -20°C. The crystallized compound **1** possesses in the monoclinic space group *P*2₁/*c* (systematic absence *hol*; *l*=*odd*, *oko*; *k*=*odd*) with *a* = 13.781(3), *b* = 9.035(1), *c* = 17.699(3) Å, β = 11.93(1)°, *V* = 2044(1) Å³, *Z* = 4 and *d*_{calc} = 1.747 g/cm³. The cell constants were determined from a least squares fit of the setting angles for 25 accurately centered reflections. X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and using the ω-2θ scan technique. A total of 4012 reflections were measured over the ranges 4 ≤ 2θ ≤ 50.0°, 0 ≤ *h* ≤ 16, -10 ≤ *k* ≤ 0 - 21 ≤ *l* ≤ 21. Three standard reflections measured every 3500 sec of X-ray exposure showed no intensity decay over the course of data collection.

The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied. Of the reflections measured a total of 3019 unique reflections with *F*² < 3σ(*F*²) were used during subsequent structure refinement.

The structure was solved by standard heavy atom Patterson techniques followed by weighted Fourier syntheses. Refinement was by full-matrix least squares techniques based on *F* to minimize the quantity ∑w(|*F*_o - |*F*_c||)² with *w* = 1/σ²(*F*). Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as constant contributions to the structure factors and were not refined. Refinement converged to *R* = 0.041 and *R*_w = 0.050.

Results and Discussion

The 1,4-diphenyltetrazenido-rhodium and iridium complexes have been prepared according to Eq. (1).



a	M=Ir	R=Ph	I
b	M=Rh	R=Ph	II
c	M=Rh	R=4-MeC ₆ H ₄	III
d	M=Ir	R=4-MeC ₆ H ₄	IV

The reaction of iridium dimer with tetrazenido dianion at room temperature gave an orange solution. It is interesting to note that Bergman and coworker¹⁵ recently reported the similar complex by the reaction of iridium imido complex with a variety of alkyl azides. The (1,2,3,4,5-pentamethylcyclopentadienyl)iridium tetraazadiene complex was isolated as air-stable orange crystal in 27% yield. The structure of compound **I** was deduced from its ¹H-NMR, IR and mass spectra. The compound **I** was robust enough to give the expected molecular ion of m/e (537) in its electron impact (70 eV) mass spectrum. The mass spectrum of **I** gave the molecular

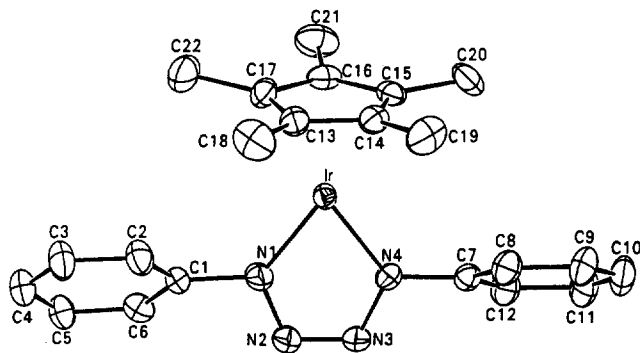


Figure 1. Structure and atom labelling of I.

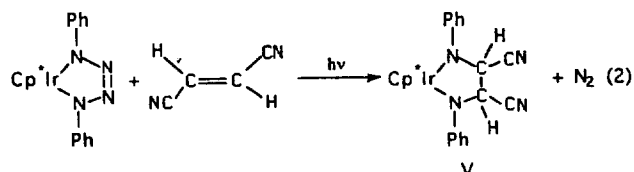
Table 1. Bond Distances (Å)

Ir-N1	1.947(6)	C1-C2	1.373(12)	C13-C14	1.437(8)
Ir-N4	1.945(6)	C1-C6	1.367(11)	C13-C17	1.407(12)
Ir-C13	2.180(8)	C2-C3	1.413(9)	C13-C18	1.486(13)
Ir-C14	2.202(7)	C3-C4	1.368(13)	C14-C15	1.418(11)
Ir-C15	2.181(7)	C4-C5	1.378(13)	C14-C19	1.496(12)
Ir-C16	2.167(8)	C5-C6	1.389(9)	C15-C16	1.407(9)
Ir-C17	2.192(8)	C7-C8	1.386(10)	C15-C20	1.507(10)
N1-N2	1.349(10)	C7-C12	1.370(11)	C16-C17	1.436(11)
N1-C1	1.465(8)	C8-C9	1.380(9)	C16-C21	1.504(13)
N2-N3	1.265(7)	C9-C10	1.393(13)	C17-C22	1.515(10)
N3-N4	1.368(9)	C10-C11	1.365(13)		
N4-N7	1.428(7)	C11-C12	1.402(9)		

Table 2. Bond Angles (°)

N1-Ir-N4	73.7(2)	N2-N3-N4	114.1(6)	C17-C13-C18	127.6(6)
N1-Ir-C13	122.6(2)	Ir-N4-N3	119.0(4)	Ir-C14-C13	70.1(4)
N1-Ir-C14	155.8(3)	Ir-N4-C7	128.0(5)	Ir-C14-C15	70.3(4)
N1-Ir-C15	164.3(3)	N3-N4-C7	112.9(6)	Ir-C14-C19	129.4(6)
N1-Ir-C16	129.0(3)	N1-C1-C2	119.1(6)	C13-C14-C15	107.7(6)
N1-Ir-C17	111.7(2)	N1-C1-C6	121.0(7)	C13-C14-C19	123.8(7)
N4-Ir-C13	148.2(2)	C2-C1-C6	119.9(6)	C15-C14-C19	128.2(6)
N4-Ir-C14	116.2(2)	C1-C2-C3	119.8(7)	Ir-C15-C14	71.9(4)
N4-Ir-C15	108.5(2)	C2-C3-C4	120.1(9)	Ir-C15-C16	70.6(4)
N4-Ir-C16	130.5(3)	C3-C4-C5	119.1(7)	Ir-C15-C20	126.5(6)
N4-Ir-C17	168.8(3)	C4-C5-C6	121.0(8)	C14-C15-C16	108.2(6)
C13-Ir-C14	38.3(2)	C1-C6-C5	120.0(8)	C14-C15-C20	126.2(7)
C13-Ir-C15	63.8(3)	N4-C7-C8	119.1(6)	C16-C15-C20	125.5(8)
C13-Ir-C16	63.7(3)	N4-C7-C12	120.6(6)	Ir-C16-C15	71.6(5)
C13-Ir-C17	37.5(3)	C8-C7-C12	120.3(6)	Ir-C16-C17	71.7(5)
C14-Ir-C15	37.8(3)	C7-C8-C9	119.9(8)	Ir-C16-C21	127.9(6)
C14-Ir-C16	63.2(3)	C8-C9-C10	120.4(8)	C15-C16-C17	108.2(7)
C14-Ir-C17	63.2(3)	C9-C10-C11	119.0(7)	C15-C16-C21	126.2(6)
C15-Ir-C16	37.8(2)	C10-C11-C12	121.1(8)	C17-C16-C21	125.2(6)
C15-Ir-C17	63.6(2)	C7-C12-C11	119.2(7)	Ir-C17-C13	70.8(4)
C16-Ir-C17	38.5(3)	Ir-C13-C14	71.7(4)	Ir-C17-C16	69.9(4)
Ir-N1-N2	120.9(4)	Ir-C13-C17	71.7(5)	Ir-C17-C22	129.2(6)
Ir-N1-C1	129.0(5)	Ir-C13-C18	127.6(6)	C13-C17-C16	107.7(5)
N2-N1-C1	110.1(6)	C14-C13-C17	108.0(7)	C13-C17-C22	129.2(8)
N1-N2-N3	112.2(6)	C14-C13-C18	124.0(7)	C16-C17-C22	122.9(8)

ion, together with M^+-N_2 ion. The photochemical excitation ($\lambda > 250$ nm) of compound I with unsaturated organic compound such as fumaronitrile led an insertion product illustrated in Eq. (2) concomitant with extrusion of N_2 . Mass spectrometry of V establishes its molecular formula as $Cp^*Ir(N_2Ph_2C_2H_2(CN)_2)$. The mass spectrum of V gave the molecular ion of m/e (587), together with the fragment ion. The presence of a new CN stretch (2162 cm^{-1}) indicates that it is an insertion complex. However, we failed to purify the product. The I-IV are quite stable but undergo slow thermal



decomposition to intractable materials. In contrast to other metal tetrazene complexes, such as the cobalt complex¹⁶, this iridium compound showed no bond cleavage chemistry upon photochemical excitation.

Crystal structure of I. The monomeric nature of I was confirmed by an X-ray diffraction study performed on a organic single crystal obtained from a benzene/hexane solution cooled to -20°C . The structure and atom labelling of I are shown in Figure 1. Selected interatomic distances and bond angles are listed in Table 1 and Table 2, respectively. Refined positional parameter is provided in Table 3. The coordination sphere of the iridium ion can be described as 2-legged

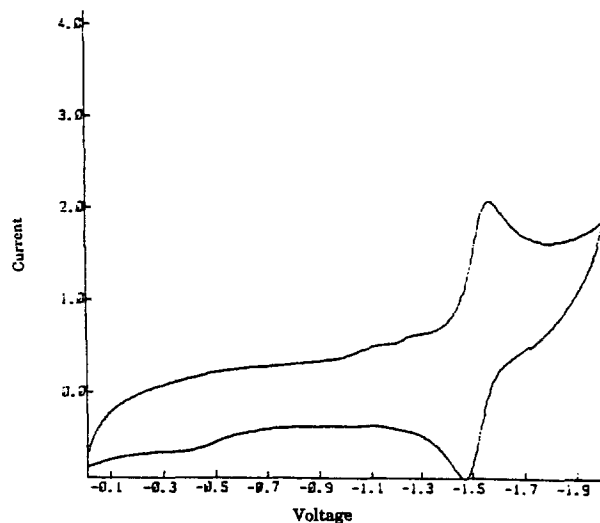
Table 3. Refined Positional Parameter

Atom	x	y	z	B_{eq} Å ²
Ir	0.18174(2)	0.21812(3)	0.51031(1)	2.659(6)
N1	0.2032(5)	0.2290(8)	0.6253(4)	3.9(1)
N2	0.1221(5)	0.2528(8)	0.6490(4)	4.0(1)
N3	0.0359(5)	0.2613(8)	0.5891(3)	3.8(1)
N4	0.0438(4)	0.2415(7)	0.5150(3)	3.1(1)
C1	0.3009(5)	0.2190(9)	0.6966(4)	3.5(2)
C2	0.3725(6)	0.112(1)	0.6985(4)	4.4(2)
C3	0.4675(6)	0.101(1)	0.7666(5)	5.1(2)
C4	0.4870(7)	0.195(1)	0.8313(5)	5.0(2)
C5	0.4128(7)	0.299(1)	0.8290(5)	4.5(2)
C6	0.3204(6)	0.312(1)	0.7614(4)	4.3(2)
C7	-0.0547(5)	0.2508(8)	0.4486(4)	3.0(1)
C8	-0.0875(5)	0.1355(9)	0.3931(4)	4.2(2)
C9	-0.1790(6)	0.145(1)	0.3271(5)	4.8(2)
C10	-0.2433(7)	0.268(1)	0.3166(6)	5.2(2)
C11	-0.2135(6)	0.378(1)	0.3734(5)	5.0(2)
C12	-0.1186(6)	0.3709(9)	0.4404(4)	4.0(2)
C13	0.2847(5)	0.0926(9)	0.4658(4)	3.6(2)
C14	0.1866(5)	0.1146(9)	0.3992(4)	3.6(2)
C15	0.1710(6)	0.2693(9)	0.3870(4)	3.5(2)
C16	0.2582(5)	0.342(1)	0.4435(4)	3.9(1)
C17	0.3300(5)	0.232(1)	0.4916(4)	3.9(2)
C18	0.3320(7)	-0.055(1)	0.4938(5)	6.4(3)
C19	0.1214(7)	-0.009(1)	0.3490(5)	6.4(2)
C20	0.0806(7)	0.343(1)	0.3213(4)	5.6(2)
C21	0.2794(7)	0.506(1)	0.4469(5)	6.1(2)
C22	0.4381(7)	0.270(1)	0.5522(6)	6.6(3)

$$B_{eq} = 4/3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha]$$

piano-stool with the η^5 -pentamethylcyclopentadienyl ligand occupying three coordinate site and the bidentate tetraazadiene ligand coordinated through the 1,4-nitrogen atoms. The metallocycle is essentially planar with the average displacement of an atom from the least-squares plane of the ring 0.015 Å; the plane is almost perpendicular to that of the cyclopentadienyl ring (dihedral angle = 87.9°).

Of particular interest is the bonding within the metallocycle. The N(2)-N(3) bond [1.267(7) Å] is considerably shorter

**Figure 2.** Cyclic voltammogram (100 mV/s scan rate) of Cp*Rh(PhN₂Ph) in 0.1 M [nBu₄N][ClO₄]-DMF electrolyte solution.

than the N(1)-N(2) [1.349(10) Å] and N(3)-N(4) [1.368(9) Å] bonds, the latter two being equivalent within the experimental error. These correspond to one double and two single nitrogen-nitrogen bonds¹⁷, respectively, as depicted in the A. Bond distances and bond angles with the metallocycle in related complexes are listed in Table 4. Relatively long Ir-N(1) [1.946(6) Å] and Ir-N(4) [1.945(6) Å] bond lengths and the planarity of the ring provide exclusive evidence for Ir-N single bonds, as a Ir-N single bond would be expected to lie within the 1.95-2.15 Å range¹⁸. Steric configuration or different conjugation with the two aryl substituents may be responsible for the small difference between the Ir-N(1) and Ir-N(4) bond lengths. The tetraazadiene ligand can be bonded in two ways represented by the formal valence structures A and B which differ with respect to the formal oxidation state of the metal. In this regard, the compound I is shown to have the formal valence structure A. It may be attributable to the large backbonding from the metal due to the pentamethylcyclopentadienyl ligand to the lowest ligand π -acceptor orbital.

Electronic Absorption Spectra. The iridium complex I displays three energy maxima at 347, 418, 642 nm. The

Table 4. Bond Distances (Å) and Bond Angles (deg) with the Metallocycles in Related Complexes, M-N(1)-N(2)-N(3)-N(4)

Complexes	M-N(1) ^a	N(1)-N(2)	N(2)-N(3)	N(1)-N(2)-N(3)	Ref.
Fe(CO) ₃ [N ₄ (CH ₃) ₂]	1.85		1.32		1
CpCo[N ₄ (C ₆ F ₅) ₂]	1.80	1.360	1.279	112.2	3(b)
{Ir[N ₄ (FC ₆ H ₄) ₂](CO)(PPh ₃) ₂ } BF ₄	1.965	1.400	1.270	112.2	4
[(3,5-MeC ₆ H ₃ N ₄ C ₆ H ₃ Me ₂ -3,5) ₂ Ni]	1.835	1.325	1.319	113.4	2
[Ni(1,4-(4-MeC ₆ H ₄) ₂ N) ₄ Cp]	1.848	1.344	1.278	113.6	8
Mo(1,4-Ph ₂ N ₄)(CO) ₂ (PPh ₃) ₂	2.086	1.33	1.33	114.0	6
Ph ₂ N ₄ SiMe ₂	1.755	1.392	1.276	111.9	20
Ni(PhN ₂ Ph)(PPh ₂ Me ₃) ₂	1.876	1.353	1.321	113.9	14
Cp*Ir(PhN ₂ Ph)	1.946	1.358	1.265	114.1	this work

^aThe average of two M-N(4) and M-N(4) bond distance

Table 5. Electrochemical Data^a for Other Process Observed for Cp*M(1,4-R₂N₄)

Compound	Solvent	E_{pa} V ^b	I_{pa}/I_{pc}
I	DMF	-1.52	0.93
II	DMF	-1.46	0.91
III	DMF	-1.48	0.96
IV	DMF	-1.42	0.92

^a Measured in 0.1 M [ⁿBu₄N][ClO₄]-DMF electrolyte solution.^b Scan rate=100 mV/s unless otherwise.

two energy transitions (347, 418 nm) can be assigned to a mixture of $d \rightarrow$ metallacycle π^* and metallacycle $\pi \rightarrow \pi^*$ transitions. These assignment is quite similar to those assigned to the complex CpCo (1,4-H₂N₄)¹⁹. The extinction coefficients (13500, 6800 M⁻¹cm⁻¹) tell us that these transition are charge-transfer bands. The transition at 642 nm is assigned to a $d-d$ transition.

Electrochemistry. Complex II displays a quasi reversible reduction in the cyclic voltammogram at a potential of -1.52 V vs an SCE reference. The voltammogram of complex II is shown in Figure 2. Electrochemical data for Cp*M (1,4-R₂N₄) is listed in Table 5. At slow scan rate (50 mV/s) the reduction of II becomes irreversible, which suggests the anion radical is unstable.

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Comparison of the Ligating Ability of Anionic Transition Metal Complex (Mn(CO)₅⁻), Transition Metal Hydrides (HCr(CO)₅⁻, HW(CO)₅⁻, cis-HW(CO)₄P(OMe)₃⁻, HFe(CO)₄⁻, trans-HFe(CO)₃P(OMe)₃⁻), and Traditional Ligands (Br⁻, P(C₆H₅)₃) to M(CO)₅⁰ (M=Cr, W)

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Heterobimetallic complexes have a donor-accepter metal-metal bond in which two electrons from the electron-rich metal moiety are donated to the other electron-deficient one. Based on the competition reactions, Cotton-Kraihanzel force constants, $\nu(\text{CO})$ IR band resolution and the relative nucleophilicity comparison of the donor ligands, the following relative ligating ability of the donor ligands toward M(CO)₅ (M=Cr, W) is assessed: $\text{cis-HW(CO)}_4\text{P(OMe)}_3^- > \text{HW(CO)}_5^- > \text{HCr(CO)}_5^- > \text{Br}^- > \text{trans-HFe(CO)}_3\text{P(OMe)}_3^- > \text{Mn(CO)}_5^- > \text{HFe(CO)}_4^- > \text{PPh}_3$

Introduction

The chemistry of the heterobimetallic complexes is a rap-

idly exploring area of inorganic and organometallic chemistry.¹ Heterobimetallic complexes with substantially different chemical properties are inherently of importance due to the