432  *Bull. Korean Chem. Soc.* **1994**, Vol. 15, No. 6

*Cheolki Paek et al.*

695.

5. Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. We used double-zeta Slater type orbitals adapted from: Clementi, E.; Roetti, C. *At. Data Nucl. Data Tables* **1974**, *14*, 177. The $H_{ij}$ values were calculated from a modified Wolfsberg-Helmholtz formula; Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. See Reference 9 for details.

6. Whangbo, M.-H. In *Electron Transfer in Biology and the Solid State: Inorganic Compounds with Unusual Properties*; King, R. B., Ed.; American Chemical Society: Washington, DC, 1990; p 269.

7. Kobayashi, H.; Takahashi, M.; Kato, R.; Kobayashi, A.; Sasaki, Y. *Chem. Lett.* **1984**, 1331.

8. (a) Mott, N. F. *Metal-Insulator Transitions*; Barnes and Noble: New York, 1977; (b) Brandow, B. H. *Adv. Phys.* **1977**, *26*, 651; (c) Whangbo, M.-H. *Acc. Chem. Res.* **1983**, *16*, 95; *J. Chem. Phys.* **1979**, *70*, 4963; (d) Whangbo, M.-H. In *Crystal Chemistry and Properties of Low-Dimensional Solids*; Rouxel, J., Ed.; Reidel: Dordrecht, The Netherlands, 1986; p 27.

9. Whangbo, M.-H; Williams, J. M.; Leung, P. C. W.; Beno, M. A.; Emge, T. J.; Wang, H. H.; Carlson, K. D.; Crabtree, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 5815.

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

Cheolki Paek, Jaejung Ko*, Sangook Kang[†], and Patrick J. Carrol[‡]

*Department of Chemical Education, Korea National University of Education, Chungbuk 363-791*

[†]*Department of Chemistry, College of National Science, Korea University, Chochiwon 339-700*

[‡]*Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323*

*Received November 24, 1993*

Monomeric rhodium and iridium-diaryltetrazene complexes Cp*M(RNN=NNR)(Cp*=1,2,3,4,5-pentamethylcyclopentadienyl; M=Rh, Ir; R=Ph, 4-tolyl) have been synthesized from [Cp*MCl$_2$]$_2$(M=Rh, Ir) and 2 equiv. of [Li(THF)$_x$]$_2$(RN$_4$R) in benzene. We have determined the crystal structure of ($\eta^5$-pentamethylcyclopentadienyl)diphenyltetrazene iridium by using graphite-monochromated Mo-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)°. 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$_2$N$_4$)(CO)$_3$] in 1967[1], 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 attacted 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 tetrazene 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. $^1$H-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 $^1$H-NMR spectra. IR spectra were obtained by using a Perkin-Elmer 1310 instrument. Mass spectra were measured on a high resolution VG70-VSEG



A                                        B
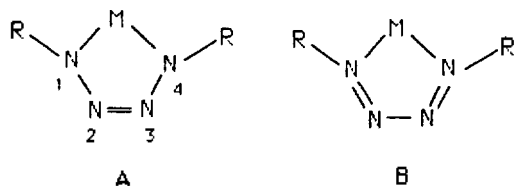
spectrometry. Cyclic voltammetry was carried out with a Potentiostat-Galvanostat Model 273 at a glassy-carbon electrode with an Ag/AgCl couple as a reference and *tetra-n*-butyl ammonium perchlorate (TBAP) as an electrolyte in $CH_3CN$. Elemental analyses were carried out at Basic Science Center. Reagent grade THF and benzene were distilled under argon from sodium-benzophenone ketyl. Pentane and hexane were distilled under Ar from sodium. $[(\eta^5-C_5Me_5)MCl_2]_2$ (M=Rh, Ir)[12], $PhN_3$[13], and $[Li(THF)_x]_2[RNN=NNR]$ (R=$C_6H_4$-$CH_3C_6$ $H_4$)[14] were prepared according to literature methods. $MCl_3\cdot$ $xH_2O$ (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 m*l*) of $[Cp*IrCl_2]_2$ (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 m*l*) dropwise. The solution was stirred at room temperature for 24 h. The volume was reduced to *ca.* 10 m*l* and the solution was filtered off. The reddish-yellow crystals were obtained by layering pentane (30 m*l*) to the solution and leaving the solution in a refrigerator at 0℃. The yield was 27%. mp. 161℃. $^1H$-NMR ($C_6D_6$): δ 7.39-7.17 (m, 10H, aromatic), 1.49 (s, 15H, $C_5Me_5$); 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$^+$-N$_2$, 54), 419 (M$^+$-PhN$_3$, 98). Anal. Calcd. for $C_{22}H_{25}IrN_4$: C, 49.16; H, 4.65. Found: C, 48.76; H, 4.49.

**Preparation of [Cp*Rh(1,4-PhN₄Ph)] (2).** To a stirred benzene solution (25 m*l*) of $[Cp*PhCl_2]_2$ (0.75 g, 1.21 mmol) was added [Li(THF)$_x$]$_2$ [PhNN=NNPh] (0.54 g, 2.42 mmol) in benzene (25 m*l*) dropwise. The solution was stirred at room temperature for 24 h. The volume was reduced to *ca.* 10m*l* and the solution was filtered off. The reddish-brown crystals were obtained by layering pentane (30 m*l*) to the solution and leaving the solution in a refrigerator at 0℃. The yield was 32%. mp. 157℃. $^1H$-NMR (CDCl$_3$): δ 7.44-7.26 (m, 10H, Ph), 1.53 (s, 15H, $C_5Me_5$); 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$^+$-N$_2$, 52), 252 (M$^+$-Ph$_2$N$_3$, 97). Anal. Calcd for $C_{22}H_{25}RhN_4$: 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℃. $^1H$-NMR (CDCl$_3$): δ 7.52-7.21 (m, 8H, aromatic), 1.42 (s, 15H, $C_5Me_5$), 1.18 (s, 6H, CH$_3$); 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$^+$-N$_2$, 48). Anal. Calcd. for $C_{24}H_{29}RhN_4$: 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℃. $^1H$-NMR (CDCl$_3$): δ

7.48-7.12 (m, 8H, aromatic), 1.39 (s, 15H, $C_5Me_5$), 1.22 (s, 6H, CH$_3$); 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$^+$-N$_2$, 56). Anal. Calcd. for $C_{24}H_{27}IrN_4$: C, 50.98; H, 5.12. Found: C, 51.36; H, 5.29.
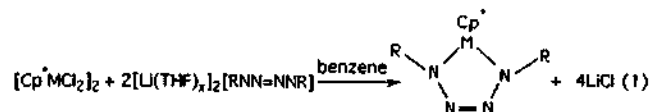
**Crystal strucutre of 1.** The crystal of **1** was grown from benzene/hexane at $-20℃$. The crystallized compound **1** possesses in the monoclinic space group $P2_1/c$ (systematic absence hol; $l=odd$, oko; $k=odd$) with $a=13.781(3)$, $b=9.035$ (1), $c=17.699(3)$ Å, $\beta=11.93(1)°$, $V=2044(1)$ Å$^3$, $Z=4$ and $d_{calc}=1.747$ g/cm$^3$. 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-$K_\alpha$ radiation ($\lambda=0.71073$ Å) and using the ω-2θ scan technique. A total of 4012 reflections were measured over the ranges $4\le2\theta\le50.0°$, $0\le h\le16$, $-10\le k\le0$ $-21\le l\le21$. 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 $F^2<3\sigma(F^2)$ 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 $\sum w(|F_o|-|F_c|)^2$ with $w=1/\sigma^2$ ($F$). Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as constant contributions to the strucutre 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).

$$[Cp^\bullet MCl_2]_2 + 2[Li(THF)_x]_2[RNN=NNR] \xrightarrow{\text{benzene}} \begin{array}{c} Cp^\bullet \\ R \diagdown \ \ \diagup M \diagdown \ \ \diagup R \\ N \diagdown N \ \ N \diagup N \\ N \!-\! N \end{array} + 4LiCl \quad (1)$$

| | | |
|---|---|---|
| a | M=Ir | R=Ph   I |
| b | M=Rh | R=Ph   II |
| c | M=Rh | R=4-MeC₆H₄   III |
| d | M=Ir | R=4-MeC₆H₄   IV |

The reaction of iridium dimer with tetrazenido dianion at room temperature gave an orange solution. It is interesting to note that Bergman and coworker[15] 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 organe 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
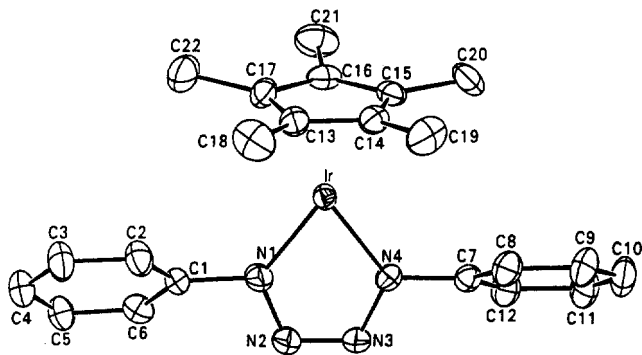
**Figure 1.** Structure and atom labelling of I.

**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) | | |

ion, together with M⁺-N₂ 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 $Cp^*Ir(N_2 Ph_2C_2H_2(CN)_2)$. 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
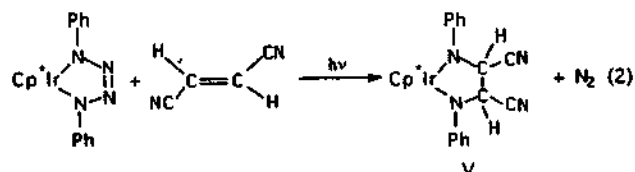


decomposition to intractable materials. In contrast to other metal tetrazene complexes, such as the cobalt complex[16], this iridium compound showed no bond cleavage chemistry upon photochemical excitation.

**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 $-20^\circ C$. 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 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) |

**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)   |

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



**Figure 2.** Cyclic voltammogram (100 mV/s scan rate) of Cp*Rh (PhN$_4$Ph) in 0.1 M [$n$Bu$_4$N] [ClO$_4$]-DMF electrolyte solution.

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

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 bonds[17], 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 range[18]. 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 Metallacylcles 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$_4$Ph)(PPh$_2$Me$_3$)$_2$ | 1.876 | 1.353 | 1.321 | 113.9 | 14 |
| Cp*Ir(PhN$_4$Ph) | 1.946 | 1.358 | 1.265 | 114.1 | this work |

$^a$The 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-R$_2$N$_4$)

| 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 [$^n$Bu$_4$N][ClO$_4$]-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 $\pi^*$ and metallacycle $\pi\rightarrow\pi^*$ transitions. These assignment is quite similar to those assigned to the complex CpCo (1,4-H$_2$N$_4$)[19]. The extinction coefficients (13500, 6800 M$^{-1}$cm$^{-1}$) 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-R$_2$N$_4$) 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.

## References

1. Dekker, M.; Knox, G. R. *J. Chem. Soc. Commun.* 1967, 1234.

2. Overbosch, P.; van Koten, G.; Overbeek, O. *J. Am. Chem. Soc.* 1980, *102*, 2091.

3. (a) Maroney, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* 1984, *106*, 4144; (b) Gross, M. E.; Trogler, W. C.; Ibers, J. A. *J. Am. Chem. Soc.* 1981, *103*, 192.

4. Einsein, F. W. B.; Sutton, D. *Inorg. Chem.* 1972, *11*, 2827.

5. Lee, S. W.; Miller, G. A.; Campana, C. F.; Maciejewski, M. L.; Trogler, W. C. *J. Am. Chem. Soc.* 1987, *109*, 5050.

6. Lee, S. W.; Trogler, W. C. *Organometallics* 1990, *9*, 1470.

7. Gross, M. E.; Trogler, W. C. *J. Organomet. Chem.* 1981, *209*, 407.

8. Overbosch, P.; van Koten, G.; Spek, A. L.; Roelofsen, G.; Duisenberg, A. J. M. *Inorg. Chem.* 1982, *21*, 3908.

9. Johnson, C. E.; Trogler, W. C. *J. Am. Chem. Soc.* 1981, *103*, 6352.

10. Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. Dalton Trans.* 1972, 1805.

11. Einstein, F. W. B.; Sutton, D. *Inorg. Chem.* 1972, *11*, 2827.

12. Kang, J. W. *J. Am. Chem. Soc.* 1969, *91*, 5970.

13. Lindsay, R. O.; Allen, C. F. H. Organic Synthesis; Willey: New York, U. S. A., 1955; Collect. Vol. IV, p 710.

14. Lee, S. W.; Miller, G. A.; Campana, C. F.; Trogler, W. C. *Inorg. Chem.* 1988, *27*, 1215.

15. Michelman, R. I.; Bergman, R. G.; Andersen, R. A. *Organometallics* 1993, *12*, 2741.

16. Trogler, W. C. *Acc. Chem. Res.* 1990, *23*, 426.

17. Veith, M. *Acta Crystallogr.* Sect. B. 1975, *31*, 678.

18. Davis, B. R.; Payne, N. C.; Ibers, J. A. *Inorg. Chem.* 1969, *8*, 2719.

19. Maroney, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* 1984, *106*, 4144.

20. Miller, G. A.; Lee, S. W.; Trogler, W. C. *Organometallics* 1989, *8*, 738.

# Comparison of the Ligating Ability of Anonic Transition Metal Complex (Mn(CO)$_5$⁻), Transition Metal Hydrides (HCr(CO)$_5$⁻, HW(CO)$_5$⁻, cis-HW(CO)$_4$P(OMe)$_3$⁻, HFe(CO)$_4$⁻, trans- HFe(CO)$_3$P(OMe)$_3$⁻), and Traditional Ligands (Br⁻, P(C$_6$H$_5$)$_3$) to M(CO)$_5$⁰ (M=Cr, W)

**Yong K. Park, In S. Han, and Marcetta Y. Darensbourg[†]**

*Department of Chemistry, Kangwon National University, Chunchenon 200-701*
*[†]Department of Chemistry, Texas A & M University, College Station, Texas 77843, U. S. A.*
*Received November 23, 1993*

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, v(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: cis-HW(CO)$_4$P(OMe)$_3$⁻, HW(CO)$_5$⁻ >HCr(CO)$_5$⁻-Br⁻>trans-HFe(CO)$_3$P(OMe)$_3$⁻>Mn(CO)$_5$⁻>HFe(CO)$_4$⁻>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