# Synthesis, Characterization, and Reactivities of Heterobimetallic $\mu$-Aryl Isocyanide Complexes with an Unusual Bridging Structure

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Reaction of $[NBu_4][W(CN)(N_2)(dppe)_2]$ with $[RuCp(\eta^6\text{-}p\text{-}FC_6H_4R)][PF_6]$ gave novel μ-aryl isocyanide complexes $[WF\{CN(\eta^5\text{-}p\text{-}C_6H_4R)RuCp\}(dppe)_2]$ (**3**) through the arylation of the CN ligand concurrent with the loss of the dinitrogen ligand. The X-ray crystallographic study of **3a** (R = H) revealed the unusual $\eta^1{:}\eta^5\text{-}\mu_2$–coordination of the phenyl isocyanide behaving as an iminocarbyne-cyclohexadienyl ligand.

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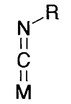
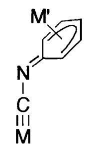
Diversity of coordination modes found in metal isocyanide complexes has been arousing considerable interest in their structures and reactivities.[1] Terminal isocyanide ligands usually bind to metals in a linear fashion (structure A). However, in complexes containing strongly π-donating metal fragments, they take a bent structure with metal-isocyanide double bond character induced by the π-back donation from the metal (structure B).[2] Now we have prepared a series of novel tungsten-ruthenium heterodinuclear complexes having bridging aryl isocyanide ligands by the arylation of an anionic tungsten cyanide with ruthenium fluoroarene complexes, which show an unique iminocarbyne structure (structure C).

(A)



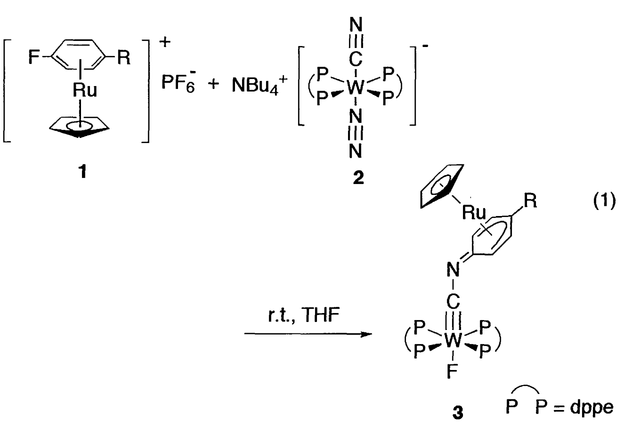
(B)



(C)

Recently we have found that an anionic dinitrogen isothiocyanato complex $[NBu_4][W(NCS)(N_2)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) reacts with ruthenium fluoroarene complexes $[RuCp(\eta^6\text{-}p\text{-}FC_6H_4R)][PF_6]$ (**1a**, R = H; **1b**, R = Me; **1c**, R = OMe; **1d**, R = COOMe; Cp = $\eta^5\text{-}C_5H_5$) to give dinuclear μ-aryldiazenido complexes $[W(NCS)\{N_2(\eta^6\text{-}p\text{-}C_6H_4R)RuCp\}(dppe)_2][PF_6]$ through the bimetallic arylation of the coordinated dinitrogen.[3] In contrast, treatment of a dinitrogen cyano complex $[NBu_4][W(CN)(N_2)(dppe)_2]$ (**2**) with complexes **1** in THF at room temperature led to the arylation of the CN ligand concurrent with the loss of the dinitrogen ligand. Repeated recrystallization from $CH_2Cl_2$-hexane gave novel μ-aryl isocyanide complexes $[WF\{CN(\eta^5\text{-}p\text{-}C_6H_4R)RuCp\}(dppe)_2]$ (**3**) as dark red crystals in 51-19% yields (eq 1). Although electrophilic alkylation of metal cyanides is a well-established route to isocyanide complexes,[4] the above reaction is noteworthy in that it provides a direct access to μ-aryl isocyanide ligands which bridge two metal centers through the isocyanide carbon and the π-coordinated arene ring.

Interestingly, complexes **3** showed no IR absorption diagnostic of terminal isocyanide ligands ($\nu(N{\equiv}C)$, 2200-1700



(1)

$cm^{-1}$).[5,6] Further spectroscopic characterization of **3** was frustrated by their limited solubility and peak broadening in the $^1H$ NMR spectrum in spite of their diamagnetism confirmed by ESR and magnetic susceptibility measurements. However, the molecular structure of $3a{\cdot}CH_2Cl_2$ (R = H) was unambiguously determined by the X-ray crystallographic study as shown in Figure 1.[7]

The most striking structural feature of **3a** is the unusual $\eta^1{:}\eta^5\text{-}\mu_2$–coordination of the phenyl isocyanide, which behaves as an iminocarbyne-cyclohexadienyl ligand. The W(1)-C(1) and C(1)-N(1) bond distances (1.841(8) and 1.348(9) Å, respectively) and the W(1)-C(1)-N(1) bond angle (169.5(6) °) clearly indicate that **3a** can be regarded as a tungsten-carbyne complex. In this context, the N(1)-C(2) bond has double-bond character which is reflected on the N(1)-C(2) distance (1.321(9) Å) and the C(1)-N(1)-C(2) angle (125.5(8) °). On the other hand, the phenyl group is coordinated to the ruthenium in an $\eta^5$-fashion.[8] The Ru-C(2) distance (2.551(8) Å) is significantly

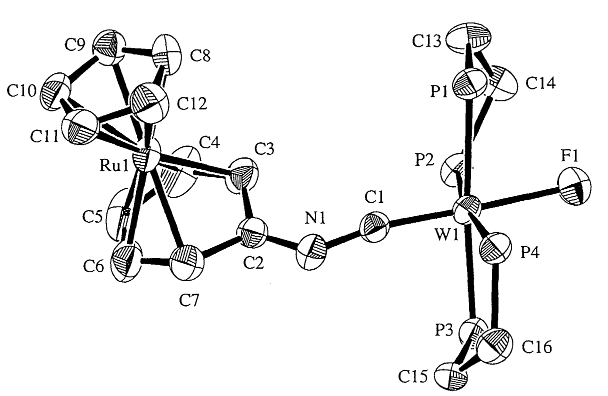
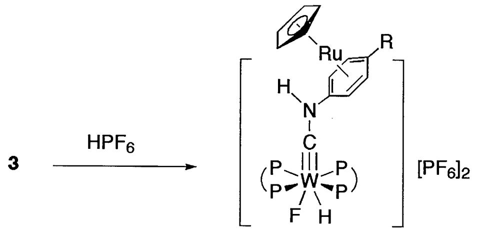


**Figure 1.** Molecular structure of $3a{\cdot}CH_2Cl_2$. Phenyl groups of the dppe ligands are omitted.

longer than the other Ru-C distances (2.14-2.24 Å), showing almost no bonding interaction. The interplanar angle between the C(3)-C(2)-C(7) plane and the pentadienyl plane is 22.5 °. All these structural parameters are in full agreement with the formulation of **3** depicted in eq 1. Such deformation of the aryl isocyanide ligand can be accounted for by the combined effects of both strong π-donation from the tungsten center and stabilization of the resulting negative charge on the aryl ring by the ruthenium center.

The aryl isocyanide ligands in complexes **3** exhibited a nucleophilic reactivity as is observed with low-valent transition metal isocyanide complexes.[9] Protonation of **3**, prepared in situ from **1** and **2**, with excess $HPF_6$ yielded the corresponding W(VI)-Ru(II) aminocarbyne-hydride complexes $[WHF\{CNH(\eta^6\text{-}p\text{-}C_6H_4R)RuCp\}(dppe)_2][PF_6]_2$ (**4**) as an orange powder or crystals (eq 2).[5,10] Complexes **4** were characterized by the $^1H$ NMR signals of WH and NH which appear at δ 2.3-3.0 as a quintet and 6.5-6.9 as a broad peak, respectively. The molecular structure of **4c** (R = OMe) was further confirmed by the X-ray diffraction study.[11] The bond distances and angles around the W-C-N moiety (W-C, 1.803(7) Å; N-C, 1.368(8) Å; W-C-N, 174.8(6) °) are typical of a tungsten-aminocarbyne complex,[9b,c] and the arene ring is bound to the ruthenium as a planar $\eta^6$-ligand. It should be noted that the structure of **4** in solution is fluxional at room temperature, judging from the $^{31}P\{^1H\}$ NMR spectrum showing only one doublet as well as the above-mentioned quintet WH signal in the $^1H$ NMR spectrum. Complex **3a** also reacted with MeI at room temperature to give the corresponding N-methylated aminocarbyne complex $[WF\{CNMe(\eta^6\text{-}C_6H_5)RuCp\}(dppe)_2]I$ (**5**), which was characterized spectroscopically.[5,12]



(2)

**4**

The present study has revealed that aryl isocyanide in a dinuclear complex containing both π-donating and electron withdrawing metal centers behaves as an unusual $\eta^1$:$\eta^5$-iminocarbyne-cyclohexadienyl ligand. Current efforts are being devoted to developing novel reactivities of the unique isocyanide ligands.

### References and Notes

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5 Satisfactory analytical data were obtained for complexes **3**, **4**, and **5**.

6 **3a**·$CH_2Cl_2$: 51%. IR (KBr) 1528, 1478, 1431, 1410 $cm^{-1}$. **3b**·$CH_2Cl_2$: 35%. IR (KBr) 1530, 1493 (sh), 1485, 1433, 1414 (sh) $cm^{-1}$. **3c**: 32%. IR (KBr) 1539, 1503, 1433, 1412, 1235 $cm^{-1}$. **3d**: 19%. IR (KBr) 1721, 1532, 1483, 1435, 1410, 1275 $cm^{-1}$.

7 Crystallographic data for **3a**·$CH_2Cl_2$: monoclinic, $P2_1/n$, $a$ = 14.408(5), $b$ = 19.751(6), $c$ = 20.407(4) Å, $\beta$ = 97.19(2) °, $V$ = 5761(2) $Å^3$, $Z$ = 4, $D_{calcd}$ = 1.561 $gcm^{-3}$, $D_{obsd}$ = 1.565 $gcm^{-3}$, $\mu(MoK_\alpha)$ = 25.08 $cm^{-1}$, $R$ = 0.041, $R_W$ = 0.029 for 5925 unique reflections with $I > 3\sigma(I)$.

8 For examples of related ruthenium-cyclohexadienyl complexes, a) S. D. Loren, B. K. Campion, R. H. Heyn, T. D. Tilley, B. E. Bursten, and K. W. Luth, *J. Am. Chem. Soc.*, **111**, 4712 (1989); b) D. J. Cole-Hamilton, R. J. Young, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, **1976**, 1995.

9 a) A. J. L. Pombeiro, in "Transition Metal Carbyne Complexes," ed by F. R. Kreißl, Kluwer Academic Publishers, Dordrecht (1993), 105; b) A. Mayr and H. Hoffmeister, *Adv. Organomet. Chem.*, **32**, 227 (1992); c) K. P. Kim and R. J. Angelici, *Adv. Organomet. Chem.*, **27**, 51 (1987).

10 **4a**: 66%. $^1H$ NMR ($CD_2Cl_2$) δ 2.33 (br qnt, $J_{P\text{-}H}$ = 38.7 Hz, 1 H), 2.77, 3.07 (br, 4 H × 2), 4.69 (d, $J$ = 5.7 Hz, 2 H), 4.81 (s, 5 H), 5.11 (t, $J$ = 5.7 Hz, 2 H), 5.21 (t, $J$ = 5.7 Hz, 1 H), 6.52 (br, 1 H), 7.1-7.4 (m, 40 H), $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) δ 42.7 (d, $J_{F\text{-}P}$ = 37 Hz, $J_{W\text{-}P}$ = 186 Hz). **4b**: 49%. $^1H$ NMR ($CD_2Cl_2$) δ 1.85 (s, 3 H), 2.29 (dqnt, $J_{P\text{-}H}$ = 39.1 Hz, $J_{F\text{-}H}$ = 2.8 Hz, 1 H), 2.77, 3.08 (br, 4 H × 2), 4.62 (d, $J$ = 6.3 Hz, 2 H), 4.75 (s, 5 H), 5.07 (d, $J$ = 6.3 Hz, 2 H), 6.51 (br, 1 H), 7.1-7.4 (m, 40 H), $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) δ 44.8 (d, $J_{F\text{-}P}$ = 35 Hz, $J_{W\text{-}P}$ = 185 Hz). **4c**: 24%. $^1H$ NMR ($CD_2Cl_2$) δ 2.42 (dqnt, $J_{P\text{-}H}$ = 39.8 Hz, $J_{F\text{-}H}$ = 3.0 Hz, 1 H), 2.78, 3.12 (br, 4 H × 2), 3.38 (s, 3 H), 4.62 (d, $J$ = 6.6 Hz, 2 H), 4.77 (s, 5 H), 5.12 (d, $J$ = 6.6 Hz, 2 H), 6.73 (br, 1 H), 7.0-7.4 (m, 40 H), $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) δ 45.4 (d, $J_{F\text{-}P}$ = 35 Hz, $J_{W\text{-}P}$ = 184 Hz). **4d**: 38%. $^1H$ NMR ($CD_2Cl_2$) δ 2.7-3.2 (m, 9 H, $CH_2$ of dppe and W-H), 3.80 (s, 3 H), 4.82 (s, 5 H), 4.86 (d, $J$ = 6.8 Hz, 2 H), 5.72 (d, $J$ = 6.8 Hz, 2 H), 6.86 (br, 1 H), 7.0-7.4 (m, 40 H), $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) δ 45.5 (d, $J_{F\text{-}P}$ = 35 Hz, $J_{W\text{-}P}$ = 181 Hz).

11 Crystallographic data for **4c**: triclinic, $P\bar{1}$, $a$ = 14.952(4), $b$ = 16.022(6), $c$ = 13.374(3) Å, $\alpha$ = 91.78(2), $\beta$ = 90.47(2), $\gamma$ = 87.89(3) °, $V$ = 3200(1) $Å^3$, $Z$ = 2, $D_{calcd}$ = 1.651 $gcm^{-3}$, $D_{obsd}$ = 1.644 $gcm^{-3}$, $\mu(MoK_\alpha)$ = 22.65 $cm^{-1}$, $R$ = 0.047, $R_W$ = 0.032 for 8467 unique reflections with $I > 3\sigma(I)$.

12 **5**·0.5($CH_2Cl_2$): 86%. $^1H$ NMR ($CD_2Cl_2$) δ 1.76 (s, 3 H), 2.46 (br, 8 H), 4.89 (s, 5 H), 5.21-5.29 (m, 4 H), 5.31 (s, 1 H, 0.5($CH_2Cl_2$)), 5.50 (t, $J$ = 5.1 Hz, 1 H), 7.0-7.4 (m, 40 H).