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Synthesis and Characterization of Binuclear Half-Sandwich Iridium and Rhodium Carbene Complexes Containing 1,2-Dichalcogenolato Carborane or Carbonato Ligands

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Summary: Reactions of bi-NHC ligands with the 16-electron half-sandwich Ir and Rh dichalcogenolato carborane complexes $Cp^*M[E_2C_2(B_{10}H_{10})]$ *(M = Ir, Rh; E = S, Se) or 16-electron half-sandwich Ir and Rh carbonate complexes* $Cp^*M(\mu\text{-}O)_2CO$ *(M = Ir, Rh) give corresponding 18-electron binuclear complexes of the type* $[\{Cp^*M(E_2C_2(B_{10}H_{10}))\}_2L]$ *(L = 1,1′-(1,2-ethanediyl)bis(3-methylimidazolin-2-ylidene); M = Ir, E = S (***4a***), Se (***4b***); M = Rh, E = S (***5a***), Se (***5b***)) and* $[Cp^*M(\mu\text{-}O)_2CO]_2L$ *(M = Ir (***8***), Rh (***9***)). Complexes* **4**−**9** *can also be obtained directly from the reactions of* $[Cp^*MCl_2]_2L$ *(M = Ir (***2***), Rh (***3***)) with* $Li_2[E_2C_2(B_{10}H_{10})]$ *or* Na_2CO_3 *in high yields. The complexes were characterized by IR, NMR spectroscopy, and elemental analysis. In addition, the molecular structures of* **4b**, **5a**, *and* **8** *have been determined by X-ray crystallography.*

N-heterocyclic carbenes (NHCs) have attracted considerable attention as a new class of ligands in organometallic coordination chemistry, due to their successful application in homogeneous catalysis especially in C−C/C−N coupling reaction and olefin metatheses.[1] NHCs can bind to both hard and soft metals, making them very versatile ligands as a result of their strong σ-donor electronic properties.[2] Although a large number of transition-metal carbene complexes have been reported,[3−5] investigations of multinuclear carbene complexes have been limited so far. Therefore, the design and synthesis of bi- and trinuclear complexes with NHCs are of considerable interest. In recent years, derivatives of 1,2-dicarba-*closo*-dodecaborane have raised attention with regard to both their fundamental properties and wide -ranging potential applications.[6] Our group and that of Herberhold et al. have reported on the synthesis of the 16-electron metal complexes $Cp^*M[E_2C_2(B_{10}H_{10})]$ (M = Ir, Rh; E = S, Se, Te) and suggested that this kind of species might be used as an acceptor, owing to the deficiency at the metal center, which has allowed the construction of special attributes, such as an addition reaction at a metal atom in a dichalcogenolato metal heterocycle.[7] Recently, a series of half-sandwich mono-, bi-, and trinuclear transition-metal complexes containing both NHCs and carborane ligands have been reported.[8]

Herein we report an easy way to synthesize binuclear transition-metal N-heterocyclic carbene complexes containing 1,2-dichalcogenolato carborane or carbonato ligands from the reactions of $[Cp^*M\{E_2C_2(B_{10}H_{10})\}]$ or $Cp^*M(\mu\text{-}O)_2CO$ (Cp^* = η^6-pentamethylcyclopentadienyl, E = S, Se; M = Ir, Rh) with silver−NHC complexes or from the reactions of $[Cp^*MCl_2]_2L$ (M = Ir, Rh; L = 1,1′-(1,2-ethanediyl)bis(3-methylimidazolin-2-ylidene)) with $Li_2[E_2C_2(B_{10}H_{10})]$ and Na_2CO_3, respectively.

Results and Discussion

The reaction of excess *N*-methylimidazole with 1,2-dibromoethane afforded the biimidazolium salts L (**1**) in high yield.[9] Transmetalation from silver−NHC complexes has proved to be an effective procedure to obtain NHC−metal complexes.[10] The reactions of the green 16-electron complexes $Cp^*M[E_2C_2(B_{10}H_{10})]$[7c,d] (E = S, Se; M = Ir, Rh) with four-electron-donor silver−NHC complexes, which were prepared by direct reaction of an imidazolium precursor and silver oxide, gave the corre-

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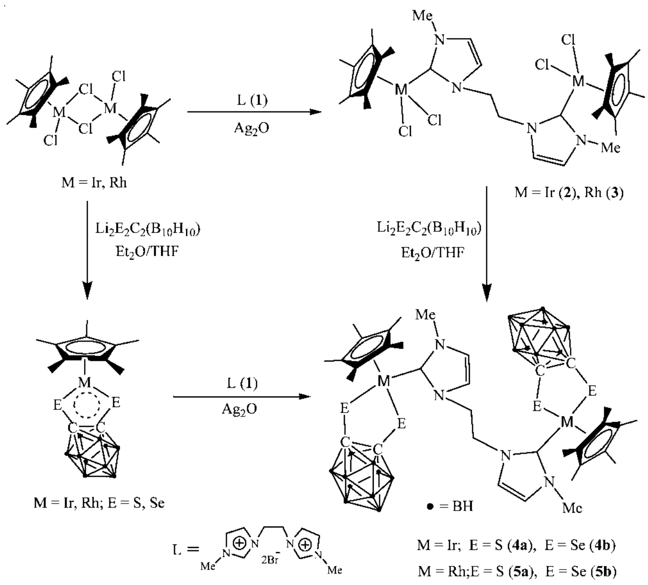
Scheme 1. Synthesis of Complexes 2, 3, 4a,b, and 5a,b



sponding 18-electron binuclear complexes [{Cp*M($E_2C_2(B_{10}H_{10})$)}$_2$L] (E = S, Se; M = Ir, Rh) (**4** and **5**) in high yields, as shown in Scheme 1.

Compounds **4** and **5** were fully characterized by IR and NMR spectroscopy and elemental analysis. The ^{1}H NMR spectra of **4** and **5** show the typical pattern of the coordinated Cp* fragment δ 1.61−1.67 ppm. The ethylene bridges appear at δ 4.6−4.7 ppm, and the equivalency signals of the imidazolyl rings appear in the ranges δ 7.05−7.15 and 7.95−8.19. The ^{11}B NMR spectra of all complexes show signals at about −6.2, −7.6, −8.7, −9.8, and −10.8 ppm in the ratio 1:1:2:4:2. In addition, the infrared spectra of complexes in the solid state exhibit intense B−H stretching of carborane at about 2575 cm^{-1}.

Crystals of **4b** and **5a** suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into concentrated solutions of the complexes in dichloromethane. As shown in Figure 1, the structure of the bimetallic complex **4b** consists of two metal atoms bridged by the ethylene−imidazolyl ligand with two parallel imidazole rings. The molecular structures confirm the six-coordinate geometry about the metal atom, assuming that the Cp* ring serves as three-coordinated ligand. The average Ir−Se distance is 2.4894 Å at the formally 18-electron metal center is significantly longer than that of corresponding 16-electron complexes, which is due to π-orbital donation of the lone pairs from the selenium atoms to the electron-deficient metal center.[3a] The Ir−C distance for the carbene ligand is 2.0176 Å, again typical for a Ir−C σ bond with very little back-donation.[8b,11,12] The bond angle C_{Cent}−Ir−C(carbene) (C_{Cent} is the central point of the Cp*) is 126.2°, thus minimizing the repulsion between the Cp* and the imidazole ring. Also, the 16-electron pseudo-aromatic metalladichalcogenolene heterocyclic system is destroyed and bent with a dihedral angle of 162.7° along the Se···Se vector for complex **4b**, which is due to the coordination of the carbene to the metal center (data for **5a** are given in the Supporting Information).

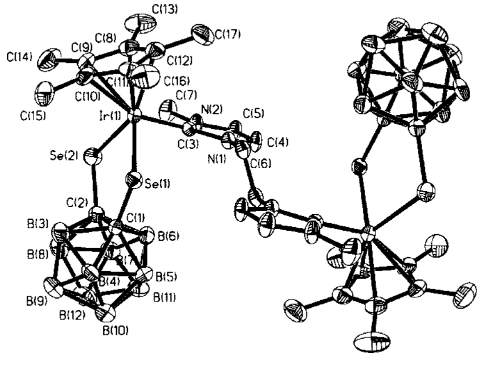
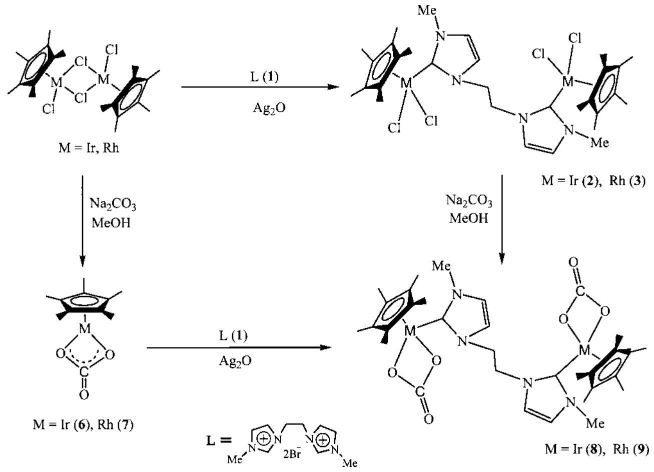


Figure 1. Molecular structure of **4b** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)−C(3) = 2.019(7), Ir(1)−Se(1) = 2.4822(9), Ir(1)−Se(2) = 2.4967(11); C(3)−Ir(1)−Se(1) = 97.07(18), C(3)−Ir(1)−Se(2) = 92.90(17), Se(1)−Ir(1)−Se(2) = 88.53(4).

Scheme 2. Synthesis of Complexes 6−9



The complexes **4** and **5** can be also prepared using another strategy. Stirring a mixture of [Cp*M(μ-Cl)Cl]$_2$ (M = Ir, Rh) with the silver−NHC species in CH_2Cl_2 at room temperature overnight produces **2** and **3**, respectively, and then treatment of **2** or **3** with $Li_2[E_2C_2(B_{10}H_{10})]$ in THF solution afforded complexes **4** and **5** in high yields, respectively.

The silver−NHC species reacted with the half-sandwich metal carbonate compounds Cp*M(μ-O)$_2$CO (M = Ir (**6**), Rh (**7**)), which were obtained from the reactions of [Cp*M(μ-Cl)Cl]$_2$ (M = Ir, Rh) in refluxing MeOH solution in the presence of Na_2CO_3,[13] to afford the binuclear complexes **8** and **9**, respectively (Scheme 2). In addition, the complexes **8** and **9** can also be obtained from the reactions of complexes **2** and **3** with Na_2CO_3 in MeOH at room temperature. The binuclear complexes **8** and **9** exhibited good solubility in organic solvents, such as CH_2Cl_2, $CHCl_3$, and THF.

Complexes **8** and **9** were characterized by IR, ^{1}H NMR, and elemental analysis. For complex **8**, the ^{1}H NMR spectrum in $CDCl_3$ shows signals at δ 1.72, 3.78, 4.50, 6.94, and 7.53 ppm, which can be assigned to the methyl groups of Cp*, methyl, CH_2CH_2, and four olefinic protons of the imidazolyl rings. The

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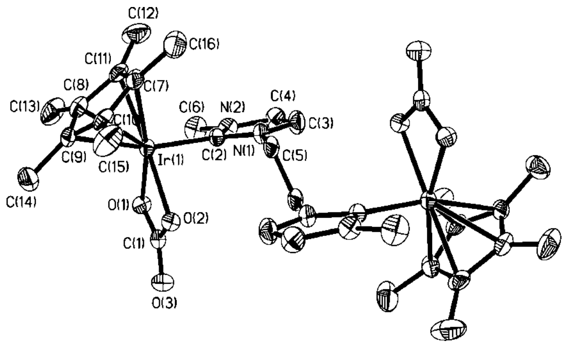

Figure 2. Molecular structure of **8** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)−C(2) = 2.037(5), Ir(1)−O(1) = 2.099(3), Ir(1)−O(2) = 2.122(3); C(2)−Ir(1)−O(1) = 86.91(17), C(2)−Ir(1)−O(2) = 87.88(18), O(1)−Ir(1)−O(2) = 62.08(13).

structure was suggested by the absorption of a single strong infrared absorption at 1626 cm^{-1}, similar to the spectral data for other μ-OCO complexes.[14]

The molecular structure of **8** was characterized by X-ray diffraction (Figure 2). The geometry around each iridium center can be described as a three-legged piano stool, which is common in Cp*Ir complexes, and the iridium atom was coordinated by a carbon of the carbene ligand and two oxygen atoms of the carbonate, which contains a four-membered ring. The distance between the iridium metal and carbon atom is 2.037(5) Å; it is compatible with typical Ir−C carbene bond lengths.[12] The bite angle of the carbonato ligand of 62.08° is quite similar to that found for related carbonate complexes.[14b]

In conclusion, a series of binuclear half-sandwich iridium(III) and rhodium(III) complexes containing both dichalcogenolate carborane or carbonate and N-heterocyclic carbene (NHC) ligands have been synthesized through two different routes. This synthetic approach, which is based upon the stepwise building up of metal complexes with NHC fragments, offers the potential for exquisite control over the detailed architecture of the materials, which may lead to a variety of unusual shapes.

Experimental Section

General Procedures. All manipulations were carried out under nitrogen using standard Schlenk and vacuum-line techniques. All solvents were purified and degassed by standard procedures. The starting materials $[Cp^*Ir(\mu\text{-}Cl)Cl]_2$,[15] $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$,[15] 1,1′-(1,2-ethanediyl)bis(3-methylimidazolium) dibromide (L),[9] and $Cp^*M[E_2C_2(B_{10}H_{10})]$ (M = Rh, Ir; E = S, Se) [7c,d] were synthesized according to the procedures described in the literature. 1-Methylimidazole was purchased from Acros. All the other reagents were commercially available and were used as received. ^1H and ^{11}B NMR spectra were obtained using a Bruker DMX-500 spectrophotometer in $CDCl_3$, for all compounds using TMS as an internal standard. IR spectra were recorded on a Niclolet AVATAR-360IR spectrometer. Element analyses were performed on an Elementar III Vario EI Analyzer.

Synthesis of Complexes 2 and 3. $(Cp^*IrCl_2)_2L$ (2). A mixture of **1**·2Br (70 mg, 0.2 mmol) and silver(I) oxide (116 mg, 0.5 mmol) was stirred for 12 h in CH_2Cl_2 (20 mL), and then a CH_2Cl_2 solution (20 mL) of $[Cp^*Ir(\mu\text{-}Cl)Cl]_2$ (160 mg, 0.2 mmol) was added. The solution was stirred at room temperature overnight and then filtered; the solvent was then evaporated to dryness under vacuum. The product was recrystallized from CH_2Cl_2/hexane to give brown crystals. Yield: 169 mg (85%). Anal. Calcd for $C_{30}H_{44}N_4Cl_4Ir_2$: C, 36.51; H, 4.49; N, 5.68. Found: C, 36.43; H, 4.64; N, 5.57. ^1H NMR (500 MHz, $CDCl_3$; δ (ppm)): 1.66 (s, $10CH_3$, 30H), 3.79 (s, $2CH_3$, 6H), 4.81 (m, $2CH_2$, 4H), 7.05 (d, imidazole, 2H), 7.35 (d, imidazole, 2H). IR (KBr; cm^{-1}): 3103 (w), 2954 (m), 2913 (m), 1604 (s), 1458 (s), 1404 (m), 1379 (m), 1241 (m), 1075 (w), 1028 (m), 775 (m), 753 (m), 696 (w), 618 (w).

$(Cp^*RhCl_2)_2L$ (3). This complex was prepared by the same procedure as described above for **2**, using $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$ (124 mg, 0.2 mmol). Yield: 145 mg (89%). Anal. Calcd for $C_{30}H_{44}N_4Cl_4Rh_2$: C, 44.58; H, 5.49; N, 6.93. Found: C, 44.46; H, 5. 46; N, 6.77. ^1H NMR (500 MHz, $CDCl_3$; δ (ppm)): 1.64 (s, $10CH_3$, 30H), 3.89 (s, $2CH_3$, 6H), 4.81 (m, $2CH_2$, 4H), 7.10 (d, imidazole, 2H), 7.51 (d, imidazole, 2H). IR (KBr; cm^{-1}): 3100 (w), 2962 (m), 2911 (w), 1581 (w), 1459 (m), 1402 (m), 1378 (m), 1241 (m), 1077 (w), 1024 (m), 775 (m), 732 (m), 689 (w), 618 (w).

Synthesis of Complexes 4a,b and 5a,b. $\{Cp^*Ir[S_2C_2(B_{10}H_{10})]\}_2L$ (4a). A mixture of **1**·2Br (70 mg, 0.2 mmol) and silver(I) oxide (116 mg, 0.5 mmol) was stirred for 10 h in CH_2Cl_2 (20 mL), and then a CH_2Cl_2 solution (20 mL) of $[Cp^*Ir\{S_2C_2(B_{10}H_{10})\}]$ (214 mg, 0.4 mmol) was added. The solution was stirred at room temperature overnight and then filtered; the solvent was then evaporated to dryness under vacuum. The product was recrystallized from CH_2Cl_2/hexane to give red crystals. Yield: 200 mg (79%). Anal. Calcd for $C_{34}H_{64}B_{20}N_4S_4Ir_2$: C, 32.47; H, 5.13; N, 4.45. Found: C, 32.65; H, 5.39; N, 4.70. ^1H NMR (500 MHz, $CDCl_3$; δ (ppm)): 1.65 (s, $10CH_3$, 30H), 3.85 (s, $2CH_3$, 6H), 4.65 (m, $2CH_2$, 4H), 7.05 (d, imidazole, 2H), 7.95 (d, imidazole, 2H). ^{11}B NMR (160 MHz, $CDCl_3$; ppm): −6.25, −7.71, −8.67, −9.95, −10.99. IR (KBr; cm^{-1}): 2578 (m) ν_{B-H}.

$\{Cp^*Ir[Se_2C_2(B_{10}H_{10})]\}_2L$ (4b). This complex was prepared by the same procedure as described above for **4a**, using **1**·2Br (70 mg, 0.2 mmol) and $[Cp^*Ir\{Se_2C_2(B_{10}H_{10})\}]$ (251 mg, 0.4 mmol). Yield: 218 mg (75%). Anal. Calcd for $C_{34}H_{64}B_{20}N_4Se_4Ir_2$: C, 28.25; H, 4.46; N, 3.88. Found: C, 27.97; H, 4.33; N, 3.51. ^1H NMR (500 MHz, $CDCl_3$; δ (ppm)): 1.67 (s, $10CH_3$, 30H), 3.83 (s, $2CH_3$, 6H), 4.60 (m, $2CH_2$, 4H), 7.06 (d, imidazole, 2H), 7.98 (d, imidazole, 2H). ^{11}B NMR (160 MHz, $CDCl_3$; ppm): −6.15, −7.81, −8.97, −9.75, −10.77. IR (KBr; cm^{-1}): 2573 (m) ν_{B-H}.

$\{Cp^*Rh[S_2C_2(B_{10}H_{10})]\}_2L$ (5a). This complex was prepared by the same procedure as described above for **4a**, using **1**·2Br (70 mg, 0.2 mmol) and $[Cp^*Rh\{S_2C_2(B_{10}H_{10})\}]$ (178 mg, 0.4 mmol). Yield: 151 mg (70%). Anal. Calcd for $C_{34}H_{64}B_{20}N_4S_4Rh_2$: C, 37.84; H, 5.98; N, 5.19. Found: C, 37.61; H, 5.72; N, 5.32. ^1H NMR (500 MHz, $CDCl_3$; δ (ppm)): 1.61 (s, $10CH_3$, 30H), 3.90 (s, $2CH_3$, 6H), 4.69 (m, $2CH_2$, 4H), 7.11 (d, imidazole, 2H), 8.19 (d, imidazole, 2H). ^{11}B NMR (160 MHz, $CDCl_3$; ppm): −6.33, −7.68, −8.73, −9.85, −10.87. IR (KBr; cm^{-1}): 2574(m) ν_{B-H}.

$\{Cp^*Rh[Se_2C_2(B_{10}H_{10})]\}_2L$ (5b). This complex was prepared by the same procedure as described above for **4a**, using **1**·2Br (70 mg, 0.2 mmol) and $[Cp^*Rh\{Se_2C_2(B_{10}H_{10})\}]$ (215 mg, 0.4 mmol). Yield: 164 mg (66%). Anal. Calcd for $C_{34}H_{64}B_{20}N_4Se_4Rh_2$: C, 32.24; H, 5.09; N, 4.42. Found: C, 32.46; H, 5.31; N, 4.83. ^1H NMR (500 MHz, $CDCl_3$; δ (ppm)): 1.66 (s, $10CH_3$, 30H), 3.87 (s, $2CH_3$, 6H), 4.70 (m, $2CH_2$, 4H), 7.15 (d, imidazole, 2H), 8.13 (d, imidazole, 2H). ^{11}B NMR (160 MHz, $CDCl_3$; ppm): −6.10, −7.56, −8.59, −9.71, −10.64, IR (KBr; cm^{-1}): 2576 (m) ν_{B-H}.

Synthesis of Complexes 6 and 7. $Cp^*Ir(\mu\text{-}O)_2CO$ (6). In a 100 mL round-bottomed flask fitted with a reflux condenser were placed $[Cp^*Ir(\mu\text{-}Cl)Cl]_2$ (160 mg, 0.2 mmol), Na_2CO_3 (53 mg, 0.5 mmol), and 30 mL of methanol as solvent. The mixture was refluxed for 2 h, after which the methanol was removed with a rotary evaporator. The reminding solid was shaken with 3 × 10 mL of

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Table 1. Crystallographic Data and Structure Refinement Parameters for Complexes 4b and 8

	4b	**8**
empirical formula	$C_{17}H_{32}B_{10}IrN_2Se_2$	$C_{36}H_{56}Cl_8Ir_2N_4O_8$
formula wt	722.67	1340.85
cryst syst, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$
a (Å)	11.215(4)	12.514(4)
b (Å)	11.238(4)	11.847(4)
c (Å)	14.053(5)	17.498(6)
α (deg)	72.147(5)	90
β (deg)	80.786(5)	108.541(4)
γ (deg)	60.952(5)	90
V (Å^3), Z	1473.6(9), 2	2459.6(15), 2
D_c (Mg/m^3)	1.629	1.811
μ(Mo Kα) (mm^{-1})	7.009	5.888
F(000)	686	1308
θ range (deg)	1.52−27.18	2.11−27.14
limiting indices	−14, to +13; −14 to +13; −18 to +11	−12 to +15; −12 to +15; −21 to +22
no. of measd/unique rflns (R(int))	7531/6344 (0.0365)	13 883/5368 (0.0425)
completeness to θ (deg)	27.18 (96.7%)	27.14 (98.6%)
no. of data/restraints/params	6344/0/304	5368/2/276
goodness of fit on F^2	0.898	0.992
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0463, wR2 = 0.0866	R1 = 0.0353, wR2 = 0.0711
R indices (all data)	R1 = 0.0742, wR2 = 0.0925	R1 = 0.0573, wR2 = 0.0781
largest diff peak/hole (e/Å^3)	2.100/−0.765	1.231/−0.995

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

CH_2Cl_2, which was then filtered. The solution was evaporated to dryness to give a dark red compound. Yield: 153 mg (98%). ^{1}H NMR (500 MHz, $CDCl_3$; δ (ppm)): 1.67 (s, CH_3). IR (KBr; cm^{-1}): 1649 (vs) ν_{OCO}.

Cp*Rh(*μ*-O)$_2$CO (7). This complex was prepared by the same procedure as described above for **6**, using [Cp*Rh(μ-Cl)Cl]$_2$ (124 mg, 0.2 mmol). Yield: 114 mg (95%). ^{1}H NMR (500 MHz, $CDCl_3$; δ (ppm)): 1.69 (s, CH_3). IR (KBr; cm^{-1}): 1647 (vs) ν_{OCO}.

Synthesis of Complexes 8 and 9. [Cp*Ir(*μ*-O)$_2$CO]$_2$L (8). A mixture of **1**·2Br (70 mg, 0.2 mmol) and silver(I) oxide (116 mg, 0.5 mmol) was stirred for 10 h in CH_2Cl_2 (20 mL), and then a CH_2Cl_2 solution (20 mL) of **6** (155 mg, 0.4 mmol) was added. The solution was stirred at room temperature overnight and then filtered; the solvent was then evaporated to dryness under vacuum. The product was recrystallized from CH_2Cl_2/hexane to give red crystals. Yield: 92 mg (48%). Anal. Calcd for $C_{32}H_{44}N_4O_6Ir_2$: C, 39.82; H, 4.60; N, 5.80. Found: C, 40.03; H, 4.34; N, 5.57. ^{1}H NMR (500 MHz, $CDCl_3$; δ (ppm)): 1.72 (s, 10CH_3, 30H), 3.78 (s, 2CH_3, 6H), 4.50 (m, 2CH_2, 4H), 6.94 (d, imidazole, 2H), 7.53 (d, imidazole, 2H). IR (KBr; cm^{-1}): 1626 (s) ν_{OCO}.

[Cp*Rh(*μ*-O)$_2$CO]$_2$L (9). This complex was prepared by the same procedure as described above for **8**, using **1**·2Br (70 mg, 0.2 mmol) and **7** (119 mg, 0.4 mmol). Yield: 69 mg (42%). Anal. Calcd for $C_{32}H_{44}N_4O_6Rh_2$: C, 48.87; H, 5.64; N, 7.12. Found: C, 48.90; H, 5.33; N, 7.30. ^{1}H NMR (500 MHz, $CDCl_3$; δ (ppm)): 1.74 (s, 10CH_3, 30H), 3.91 (s, 2CH_3, 6H), 4.45 (m, 2CH_2, 4H), 6.98 (d, imidazole, 2H), 7.55 (d, imidazole, 2H). IR (KBr; cm^{-1}): 1629 (s) ν_{OCO}.

X-ray Structure Determination. Diffraction data of **4b**, **5a**, and **8** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). All the data were collected at room temperature, and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL).[16] SADABS[17] absorption corrections were applied to the data, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. All calculations were performed using the Bruker program Smart. A summary of the crystallographic data and selected experimental information are given in Table 1.

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Supporting Information Available: CIF files giving crystallographic data for **4b**, **5a**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800694H

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