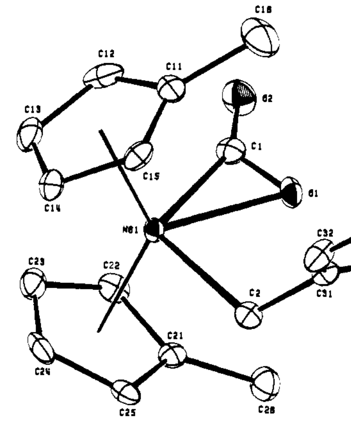


Figure 1. ORTEP plot of **2a**.

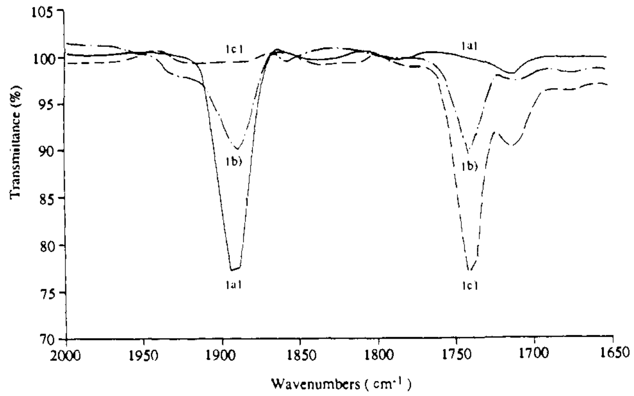


Figure 2. IR spectra: (a) (—) **1a** (0.36 mmol) in $PhCH_3$ under N_2; (b) (•••) **1a** + 0.090 mmol of $O_2 \rightarrow$ **1a** + **2a**; (c) (- - -) **1a** + 0.180 mmol of $O_2 \rightarrow$ **2a**. The absorption at 1710 cm^{-1} in a–c is from incomplete solvent subtraction or an impurity in **1a**.

That the additional oxygen atom in **2a** was derived from dioxygen was clearly established by isotopic labeling. Thus, reaction of **1a** with $^{18}O_2$ (99%) produced >90% $(\eta^5\text{-}C_5H_4CH_3)_2Nb(C^{18}O^{16}O)CH_2Ph$ (**2a***) as determined by MS analysis.[12] Interestingly, the IR spectrum of **2a*** indicated that the ^{18}O label was almost equally distributed between the coordinated and uncoordinated oxygen atoms of the $\eta^2\text{-}CO_2$ ligand.[12] Scrambling of the label is not the result of postoxidation ligand exchange since no incorporation of $C^{16}O_2$ occurred when a toluene solution of **2a*** was stirred under 1 atm of $C^{16}O_2$ for 20 h. These results are consistent either with an oxidation pathway involving a symmetrically bound CO_2 intermediate of a fluxional process for product **2a*** causing interchange of the oxygen atoms.

The stoichiometry of the reaction was determined by titrating a toluene solution of **1a** (0.36 mmol) with oxygen. IR analysis (Figure 2) showed that addition of 2.0 mL (0.090 mmol) of O_2 (by gas syringe) caused ca. 50% conversion of **1a** to **2a**; addition of another 2.0 mL of oxygen resulted in total disappearance of the remaining **1a** within 5 min. Thus, the reaction of **1** with oxygen proceeds according to eq 1 *with incorporation of both oxygen atoms of O_2 into the product* **2**.

$$2(\eta^5\text{-}C_5H_4CH_3)_2Nb(CO)R + O_2 \rightarrow 2(\eta^5\text{-}C_5H_4CH_3)_2Nb(\eta^2\text{-}CO_2)R \quad (1)$$

1 2

In a preliminary assessment of the generality of the metal-mediated carbon monoxide oxidation process, a number of related carbonyl complexes were screened for oxygen reactivity. Thus, treatment of a toluene solution of $(\eta^5\text{-}C_5H_4CH_3)_2Nb(CO)R$ (**1b–d**; R = $CH_2Si(CH_3)_3$, $CH_2C(CH_3)_3$, CH_3) with O_2 (1 atm, 20 °C) generated the corresponding CO_2 complexes $(\eta^5\text{-}C_5H_4CH_3)_2Nb(\eta^2\text{-}CO_2)R$ (**2b–d**[8,11]) in high yield (80–95%). Similarly, when a THF solution of $(\eta^5\text{-}C_5H_5)_2Mo(CO)$[15] was exposed to O_2 (1 atm) at 0 °C, the carbonyl absorption at 1914 cm^{-1} disappeared within minutes and about 10% $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$[13] and 18% $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_3)$[16] were generated along with $(\eta^5\text{-}C_5H_5)_2MoO$. Since $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ undergoes thermal disproportionation only slowly under these conditions,[16] the carbonate complex formed may be derived from oxygen oxidation of $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$.

These findings not only afford new insight into the possible role of metal–CO_2 complexes in catalytic CO oxidation but also offer a new, convenient synthetic route to such complexes.[17] Studies are underway to establish the scope and mechanistic details of these reactions.

Acknowledgment. We are grateful for support provided by the U.S. Department of Energy, Office of Basic Energy Sciences (89ER13997).

Supplementary Material Available: Preparative and spectroscopic data for compounds **1a–d** and **2a–d**, tables of positional and thermal parameters, and tables of interatomic distances and angles (8 pages); table of observed and calculated structure factors for **2a** (10 pages). Ordering information is given on any current masthead page.

---

(11) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145.

(12) MS (12 eV, EI, *m/e*) of **2a***: 358 (25) $\{(C_5H_4CH_3)_2Nb(^{16}O)CH_2Ph^+\}$, 360 (25) $\{(C_5H_4CH_3)_2Nb(^{18}O)CH_2Ph^+\}$; the IR of **2a*** had nearly equal intensity absorptions at 1732 ($C{=}^{16}O$) and 1713 cm^{-1} ($C{=}^{18}O$) in toluene (1704 and 1675 cm^{-1} in KBr). A comparable solution/KBr IR shift also has been noted for $Cp_2Mo(\eta^2\text{-}CO_2)$.[13] Most $\eta^2\text{-}CO_2$ complexes, like **2**, exhibit a strong $\nu(CO)_{asym}$ and a very weak or nonobservable $\nu(CO)_{sym}$.[11,13,14]

(13) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985.

(14) Jegat, C.; Fouassier, M.; Mascetti, J. *Inorg. Chem.* **1991**, *30*, 1521.

(15) Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1978**, *17*, 2410.

(16) Belmore, K. A.; Vanderpool, R. A.; Tsai, J.-C.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004.

(17) Reviews: (a) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: W. Germany, 1988. (b) Ito, T.; Yamamoto, A. In *Organic and Bioorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Halstead Press: New York, 1982; Chapter 3, pp 79–151. (c) Darensbourg, D.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129.

Silylcarbocyclization Reactions Catalyzed by Rh and Rh–Co Complexes

Iwao Ojima,* Robert J. Donovan, and William R. Shay

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794-3400

Received March 18, 1992

In the course of our study on the mechanism, scope, and limitation of "silylformylation", which was discovered independently by Matsuda et al.[1] and by us,[2] we isolated a small amount of 2,5-dibutyl-3-(dimethylphenylsilyl)-2-cyclopenten-1-one (**1a**) as a side product in the reaction of 1-hexyne with dimethylphenylsilane catalyzed by $Co_2Rh_2(CO)_{12}$ or $Rh_4(CO)_{12}$.[3] Under more optimized conditions, e.g., triethylsilane/$(t\text{-}BuNC)_4RhCo(CO)_4$[4] at 60 °C, cyclopentenone **1b** ($R_3Si = Et_3Si$) was obtained as the major product in 54% yield (eq 1). In order to accommodate this unique cyclization, it was reasonable to assume that the

---

(1) (a) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332. (b) Matsuda, I.; Ogiso, A.; Sato, S. *J. Am. Chem. Soc.* **1990**, *112*, 6120.

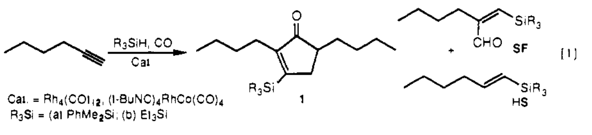
(2) (a) Ojima, I. 22nd Organosilicon Symposium, April 7–8, 1989, Philadelphia, PA, Abstracts, Plenary 7. (b) Ojima, I.; Ingallina, P. 23rd Organosilicon Symposium, April 20–21, 1990, Midland, MI, Abstracts G2.

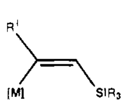
(3) Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38.

(4) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1991**, *10*, 3211.

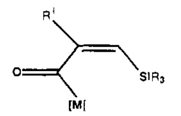
0002-7863/92/1514-6580$03.00/0

β-silylacryloyl[M] intermediate **3** (M = RhCo), which was generated via β-silylethenyl[M] complex **2**, was trapped by an olefinic species such as 2-silyl-1-hexene.[3]





2

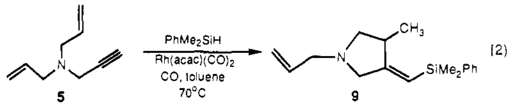


3

If this is the case, we should be able to trap **3** with externally added alkenes, and such a reaction would be potentially very useful as a new synthetic method. However, attempted trapping of **3** with a variety of alkenes was unsuccessful. Accordingly, we investigated an intramolecular trapping of a β-silylacryloyl[M] species or β-silylethenyl[M] species by using allyl propargyl ether (**4**) diallylpropargylamine (**5**), and allyldipropargylamine (**6**) as substrates, which led to the discovery of novel silylcarbocyclization (SiCAC) reactions. We communicate here our preliminary study on two types of such SiCAC reactions.

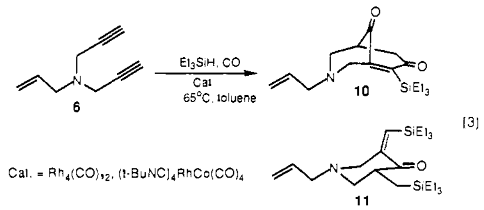
The reaction of allyl propargyl ether (**4**, 4.0 mmol) with dimethylphenylsilane (4.0 mmol) catalyzed by $Rh_4(CO)_{12}$ (0.04 mmol, 1.0 mol %) was carried out in toluene (15 mL) at 70 °C and ambient pressure of CO for 18 h to give 3-(silylmethylene)-4-methyltetrahydrofuran (**7**) in 61% yield as the sole product through a novel silylcarbocyclization (SiCAC).[5] It is apparent that **7** is formed via the intramolecular trapping of β-silylethenyl[M] intermediate **4A** with the ethenyl moiety, followed by hydride shift (Scheme I). Since this SiCAC reaction (type 1-SiCAC) should not require carbon monoxide, we carried out the reaction under nitrogen. In fact, when $Rh(acac)(CO)_2$ was used as a catalyst under nitrogen, **7** was obtained in 85% yield accompanied by a small amount of hydrosilylation product, (*E*)-1-(dimethylphenylsilyl)-4-oxa-1,6-heptadiene (**8**) (<10%).[6]

The type 1-SiCAC reaction was further applied to diallylpropargylamine (**5**) by using $Rh(acac)(CO)_2$ at 70 °C and ambient pressure of carbon monoxide to give the corresponding pyrrolidine **9** exclusively in nearly quantitative yield (eq 2).[5]



SiCAC-paper-1 3/13/92 3:22 PM

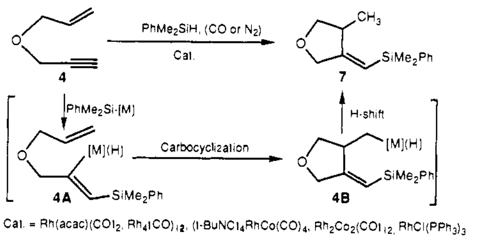
Next, the reaction of allyldipropargylamine (**6**, 4.0 mmol) with triethylsilane (12.0 mmol) catalyzed by $(t\text{-}BuNC)_4RhCo(CO)_4$ (0.01 mmol, 0.25 mol %) was carried out in toluene (15 mL) at 65 °C and 50 atm of CO in an autoclave for 48 h. The reaction gave a unique SiCAC product with incorporation of two CO (**10**) as the predominant product (62%) accompanied by a small amount of another SiCAC product with single CO incorporation (**11**) (<2%) (type 2-SiCAC) (eq 3). When the reaction was carried out using $Rh_4(CO)_{12}$ at 65 °C and ambient pressure of CO, **11** was obtained as virtually the sole product (81%).[5]



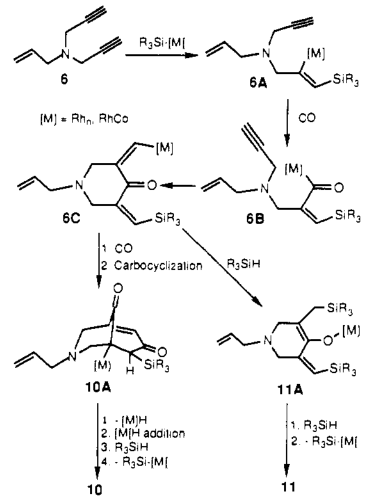
The results clearly indicate that the β-silylacryloyl[M] intermediate **6B** was exclusively trapped by the alkyne moiety, leaving the alkene moiety intact. It should be noted that CO insertion into the carbon–metal bond of **6A** is much faster than intramolecular trapping by the alkyne or the alkene moiety. The formation of **10** should include the second CO insertion, carbocyclization,[7] β-hydride elimination of [M]H, and regioselective addition of [M]H followed by regeneration of $R_3Si[M]$, yielding **10**. In a similar manner, **11** should be formed through a metal enolate **11A**, followed by regeneration of $R_3Si[M]$. The proposed mechanisms are illustrated in Scheme II.

The results described above clearly indicate that the cyclopentenones **1** were formed through the *intermolecular* trapping of β-silylacryloyl[M] species **3** with another molecule of 1-hexyne, followed by carbocyclization and regioselective reduction in a manner very similar to that for the formation of **10**. To the best of our knowledge, the type 1-SiCAC reaction is the first example for efficient trapping of a β-silylethenyl–metal species by an alkene and the type 2-SiCAC reaction is the first example for efficient trapping of a β-silylacryloyl–metal species by an alkyne.[8] Since

Scheme I



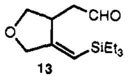
Scheme II



---

(5) The assignment of *E* stereochemistry for **7** and **9** and *Z* stereochemistry for **11** is tentative on the basis of the established syn addition of alkynes to the Si–[M] bond in silylformylation.[1,3] **Note Added in Proof**: 1D NOE and NOESY experiments have revealed that the stereochemistry of **11** is *E*, which strongly suggests the occurrence of *Z* to *E* isomerization in the same manner as that observed in the hydrosilylation of 1-alkynes, see: Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127.

(6) Other catalysts (0.1 mol %) are also active for this type 1-SiCAC reaction, giving **7** under nitrogen at 70 °C for 16–24 h: $Rh(acac)(CO)_2/Cy_3P$, 86%; $(t\text{-}BuNC)_4RhCo(CO)_4$, 72%; $Rh_4(CO)_{12}$, 77%; $RhCl(PPh_3)_3$, 82%; $Co_2Rh_2(CO)_{12}$, 72%. When the reaction was carried out under higher CO pressure (10 atm) using triethylsilane, CO insertion into **4B** took place, giving the corresponding aldehyde **13** as a minor product (15–20%) together with a silylformylation product (70–75%).



13

(7) For leading papers on carbocyclizations and carbometalation–cyclizations, see: (a) Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34. (b) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65. (c) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (d) Takacs, J. M.; Zhu, J.; Chandramouli, S. *J. Am. Chem. Soc.* **1992**, *114*, 773. (e) RajanBabu, T. V.; Nugent, W. A.; Taber, D. F.; Fagan, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7128. (f) Lund, E. C.; Livinghouse, T. *J. Org. Chem.* **1989**, *54*, 4487. (g) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.

these novel SiCAC reactions have high synthetic potential, further investigations on the mechanism, organometallic chemistry, and applications to organic syntheses are actively underway.

Acknowledgment. This research was supported by grants from the National Science Foundation and the National Institutes of Health. A generous support from Mitsubishi Kasei Corporation is gratefully acknowledged. The authors (R.J.D. and W.R.S.) thank Dr. Zhaoda Zhang for his helpful discussions as well as technical assistance.

Supplementary Material Available: Identification data for **7**, **9**, **10**, **11**, and **13**, including 2D NMR spectra, i.e., COSY and HETCOR, for **10** and **11** (7 pages). Ordering information is given on any current masthead page.

---

[8] The intramolecular trapping of a β-silylethenyl–nickel species by an alkyne moiety in 1,7-octadiyne and related systems, giving the corresponding carbocyclization product, was reported by Tamao et al. See: Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 6478.

(1,5-Cyclooctadiene)bis(3,6-di-*tert*-butylcatecholato)-iridium(IV). An Organometallic Aryl Oxide Complex with a Charge-Transfer Transition at Unusually Low Energy

Christopher W. Lange and Cortlandt G. Pierpont*

Department of Chemistry and Biochemistry
University of Colorado, Boulder, Colorado 80309

Received February 19, 1992

Many of the interesting and important features of transition metal complexes containing catecholate and semiquinone ligands are related to the similarity in energy between quinone π^*-orbitals and the metal d-levels. In some cases this property is responsible for intense, low-energy charge-transfer transitions that sometimes extend well into the near-infrared NIR region.[1] Characterization on the "bending crystals" of $Rh(CO)_2$(3,6-di-*tert*-butylsemiquinone) has shown that a low-energy metal–ligand charge-transfer transition associated with stacked oligomers of complex units contributes to unique photomechanical properties in the solid state.[2] The higher d-orbital energy of iridium may result in charge-transfer transitions shifted further to lower energy, resulting in compounds with high optical sensitivity in the infrared. We now describe an unusual product obtained by the addition of cobaltocenium 3,6-di-*tert*-butylsemiquinone to $[Ir(1,5\text{-COD})Cl]_2$.

The anticipated product of the synthetic procedure was Ir(1,5-COD)(3,6-DBSQ).[3] However, crystallographic characterization on the dark red complex obtained from this reaction showed that the product was actually $Ir(1,5\text{-COD})(3,6\text{-DBCat})_2$ with the structure shown in Figure 1.[4] The Ir(IV) formulation for the complex in the solid state is consistent with the structural features of the quinone ligands. Ring C–C lengths reflect the expected aromatic structure of a catecholate ligand, and the C–O lengths are of values that are longer than semiquinone lengths.[5] In particular, the length to O1 is 1.35 (1) Å, while the length to O2, trans to the COD olefin bond, is 1.32 (1) Å. In toluene solution at room temperature, the $S = {}^1/_2$ complex molecule shows a broad EPR resonance centered about a g-value of 1.986 which is approximately 200 G in width. In frozen toluene at 77 K, the signal splits to give a slightly rhombic spectrum with components $g_1 = 1.948$, $g_2 = 1.952$, and $g_3 = 2.006$. No hyperfine structure is observed for either the isotropic or anisotropic spectrum. Electrochemical characterization on $Ir(1,5\text{-COD})(3,6\text{-DBCat})_2$ shows that the complex undergoes reversible one-electron oxidation and reduction reactions.[6] Couples are closely spaced at potentials of −0.092 V and −0.636 V (vs Fc^+/Fc), respectively, and the complex may be chemically oxidized with $Ag(PF_6)$ and reduced with cobaltocene.

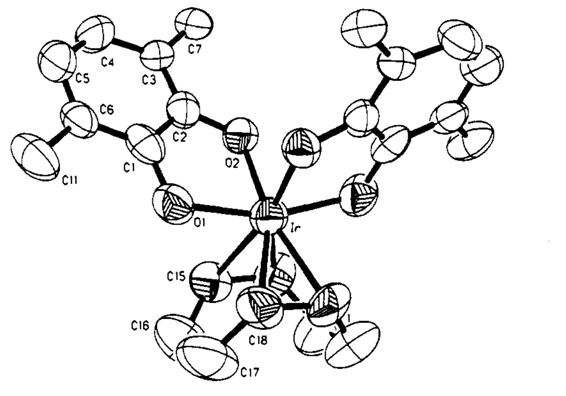


Figure 1. View showing the structure of $Ir(1,5\text{-COD})(3,6\text{-DBCat})_2$. A crystallographic 2-fold axis passes between the olefin groups and relates the two catecholate ligands. Selected bond lengths (Å): Ir–O1 2.014 (7), Ir–O2 2.014 (6), Ir–C15 2.207 (11), Ir–C18 2.192 (9), C1–O1 1.352 (13), C2–O2 1.318 (12), C15–C18′ 1.413 (17).

Figure 2 shows the infrared spectrum obtained for the complex.[7] The sharp bands at lower energy are the usual ligand vibrations, but the broad, intense transition centered near 4200 cm^{-1} is an electronic absorption. The band appears unsymmetrical in the figure due to moisture in the KBr matrix; in toluene solution at room temperature it appears as a single symmetrical transition at 2340 nm with a molar extinction coefficient of 5100 $M^{-1}\,cm^{-1}$. Assignment of this transition is not unambiguous. It may simply be a metal–catecholate charge-transfer transition,[8] but other possibilities exist. Intense, low-energy interligand charge-transfer transitions commonly occur for members of the ML_2(3,5-DBCat)(3,5-DBCat) series, with M = Ru and Os and L_2 = bpy, $2PPh_3$, and 2CO.[9,10] This requires significant mixing with an Ir(III) charge-localized form of the complex, Ir(1,5-COD)(3,6-DBSQ)(3,6-DBCat). The electrochemistry supports this in ap-

---

[1] Haga, M.; Dodsworth, E. S.; Lever, A. B. P.; Boone, S. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1986**, *108*, 7413.

[2] Lange, C. W.; Foldeaki, M.; Nevodchikov, V. I.; Cherkasov, V. K.; Abakumov, G. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1992**, *114*, 4220.

[3] Synthesis of $Ir(1,5\text{-COD})(3,6\text{-DBCat})_2$: $[Ir(1,5\text{-COD})Cl]_2$ (0.153 g, 0.23 mmol) dissolved in 5 mL of CH_2Cl_2 was added to a solution of $[Co(Cp)_2](3,6\text{-DBSQ})$ prepared by combining cobaltocene (0.091 g, 0.48 mmol) and 3,6-di-*tert*-butyl-1,2-benzoquinone (0.10 g, 0.47 mmol) in 10 mL of CH_2Cl_2. The mixture became dark red, and a brown precipitate separated from the solution. The precipitate was collected by filtration, and the red filtrate was slowly evaporated under a flow of N_2. Dark red crystals of $Ir(1,5\text{-COD})(3,6\text{-DBCat})_2$ were obtained from the evaporated filtrate in yields that have varied from 30% to 50%. The brown precipitate has not yet been identified. Details of the reaction and products will be published separately.

[4] X-ray analysis of $Ir(1,5\text{-COD})(3,6\text{-DBCat})_2$: tetragonal, space group $P4_32_12$; $a = 15.007$ (2) Å, $c = 15.234$ (4) Å, $V = 3431$ (1) $Å^3$, $Z = 4$; $R = 0.040$ for 2261 unique observed reflections. Details of the structure determination are given in the supplementary material.

[5] (a) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 44. (b) Carugo, O.; Castellani, C. B.; Djinovic, K.; Rizzi, M. *J. Chem. Soc., Dalton Trans.* **1992**, 837.

[6] Cyclic voltammograms were recorded in acetonitrile solution using tetrabutylammonium hexafluorophosphate as electrolyte. An Ag/Ag^+ reference electrode was used, and the cobaltocenium/cobaltocene couple was used as an internal standard (−1.318 V vs Fc^+/Fc).

[7] IR (KBr) ν (between 1000 and 1600 cm^{-1}): 1552 (s), 1480 (m), 1466 (m), 1402 (s), 1384 (m), 1353 (m), 1307 (s), 1284 (s), 1212 (m), 1151 (s) cm^{-1}. UV–vis–NIR (toluene): 292 (9200 $M^{-1}\,cm^{-1}$), 475 (2600), 513 (2600), 564 (1800), 854 (460), 975 (390), 1304 (480), 2340 (5100) nm.

[8] (a) Ernst, S.; Hanel, P.; Jordanov, J.; Kaim, W.; Kasack, V.; Roth, E. J. *J. Am. Chem. Soc.* **1989**, *111*, 1733. (b) Haga, M.; Isobe, K.; Boone, S. R.; Pierpont, C. G. *Inorg. Chem.* **1990**, *29*, 3795. (c) Dei, A.; Gatteschi, D.; Pardi, L.; Russo, U. *Inorg. Chem.* **1991**, *30*, 2589.

[9] Lever, A. B. P.; Auburn, P. R.; Dodsworth, E. S.; Haga, M.; Liu, W.; Melnik, M.; Nevin, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 8076.

[10] (a) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 35. (b) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1991**, *30*, 2906. (c) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.*, submitted for publication.

0002-7863/92/1514-6582$03.00/0