

Nickel, Palladium, and Platinum Complexes of η^5 -Cyclopentadienide $C_{60}R_5$ Ligands. Kinetic and Thermodynamic Stabilization Effects of the $C_{60}Ph_5$ Ligand

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The nickel-, palladium-, and platinum-RFCp complexes $Ni(\eta^5\text{-RFCp})(\eta^3\text{-allylic})$ (**3b**, RFCp = $C_{60}R_5$, R = Me, allylic = methallyl; **4a**, R = Ph, allylic = allyl; **4b**, R = Ph, allylic = methallyl), $Pd(\eta^5\text{-RFCp})(\eta^3\text{-allylic})$ (**7a**, R = Me, allylic = allyl; **7b**, R = Me, allylic = methallyl; **7c**, R = Me, allylic = crotyl; **8a**, R = Ph, allylic = allyl; **8b**, R = Ph, allylic = methallyl; **8c**, R = Ph, allylic = crotyl), and $Pt(\eta^5\text{-RFCp})(\eta^3\text{-methallyl})$ (**9**, R = Me; **10**, R = Ph), were synthesized by transmetalation between $K(\text{RFCp})$ (R = Me, Ph) and $[Ni(\text{allylic})\text{-Br}]_2$, $[Pd(\text{allylic})Cl]_2$, or $[Pt(\text{methallyl})Cl]_2$ in THF at 25 °C for 10 min. The nickel-PhFCp complexes **4a,b** are unusually more stable toward molecular oxygen than the corresponding simple nickel cyclopentadienides and survive in air for many hours at elevated temperature. The crystal structures and the electrochemical properties of the palladium complexes suggest that the unusual stability of the PhFCp complexes is due to the kinetic stabilization effect of the five Ph groups surrounding the metal atom and the thermodynamic stabilization effect of the electron-withdrawing fullerene moiety, hence suggesting new opportunities for the synthesis of otherwise unstable organometallic compounds.

Introduction

The electronic structure of the ligand is the major factor that controls the reactivity and stability of transition-metal complexes: an illustrative example is the 18-electron sandwich complex of iron(II), ferrocene, where a pair of 6- π -electron cyclopentadienide ligands endow the complex with extremely high stability.¹ The sandwich structure may not be enough for the stability, since ferrocene's immediate neighbor, 20-electron nickelocene, is relatively unstable and susceptible to oxidation by molecular oxygen.² The 18-electron nickel π -allyl cyclopentadienyl complex $Ni(\eta^5\text{-Cp})(\eta^3\text{-allyl})$ is even more unstable to oxygen and immediately decomposes upon exposure to air.^{3,4} The physical structure of the ligand is another controlling factor. Suitably designed bulky ligands are known to stabilize coordinatively

unsaturated metal complexes by shielding the space around the metal atom. Isopropyl-substituted tris-(pyrazolyl)borate is a recent example of such ligands.^{5,6}

We previously reported the synthesis of a series of η^5 metal compounds that bear a $C_{60}R_5$ cyclopentadienyl ligand (generically denoted as FCp ligands):⁷ $Re(\eta^5\text{-}C_{60}R_5)(CO)_3$,⁸ $Fe(\eta^5\text{-}C_{60}Me_5)(\eta^5\text{-}C_5H_5)$,⁹ $Ru(\eta^5\text{-}C_{60}Me_5)\text{-}L_n$,^{10,11} and $Rh(\eta^5\text{-}C_{60}Me_5)(CO)_2$.¹² ($C_{60}Me_5$ is abbreviated as MeFCp). We have so far synthesized MeFCp complexes or, in one case, FCp ligands bearing hydrogen atoms.^{8,13} Though we reported the synthesis of the $C_{60}\text{-}Ph_5$ ligand (PhFCp) and its thallium complex several years ago,^{7a} we have so far been unable to synthesize

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(1) (a) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039. (b) Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 632. (c) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125. (d) Fischer, E. O.; Pfaff, W. Z. *Z. Naturforsch.* **1952**, *7B*, 377.

(2) Wilke, G.; Jolly, P. W. *The Organic Chemistry of Nickel*; Academic Press: New York, London, 1974; Vol. 1 (Organonickel Complexes), p 422.

(3) (a) Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon: New York, 1982; Vol. 6. (b) Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Eds. *Comprehensive Organometallic Chemistry II*; Pergamon: New York, 1995; Vol. 9.

(4) (a) Fischer, E. O.; Bürger, G. *Chem. Ber.* **1961**, *94*, 2409. (b) McClellan, W. R.; Hoehn, H. H.; Cripps, H. N.; Muettterties, E. L.; Howk, B. W. *J. Am. Chem. Soc.* **1961**, *83*, 1601.

(5) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419. (c) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

(6) (a) Bruce, M. I.; Ostaszewski, A. P. *P.* **1973**, 2433. (b) Abu Salah, O. M.; Bruce, M. I.; Hameister, C. *Inorg. Synth.* **1982**, *21*, 107.

(7) (a) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850. (b) Sawamura, M.; Iikura, H.; Ohama, T.; Hackler, U. E.; Nakamura, E. *J. Organomet. Chem.* **2000**, *599*, 32. (c) Sawamura, M.; Toganoh, M.; Kuninobu, Y.; Kato, S.; Nakamura, E. *Chem. Lett.* **2000**, 270.

(8) Toganoh, M.; Matsuo, Y.; Nakamura, E. *Angew. Chem., Int. Ed.* **2003**, *42*, 3530.

(9) Sawamura, M.; Kuninobu, Y.; Toganoh, M.; Matsuo, Y.; Yamanaoka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2002**, *124*, 9354.

(10) Matsuo, Y.; Nakamura, E. *Organometallics* **2003**, *22*, 2554.

(11) Matsuo, Y.; Kuninobu, Y.; Ito, S.; Nakamura, E. *Chem. Lett.* **2004**, *33*, 68.

(12) Sawamura, M.; Kuninobu, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2000**, *122*, 12407.

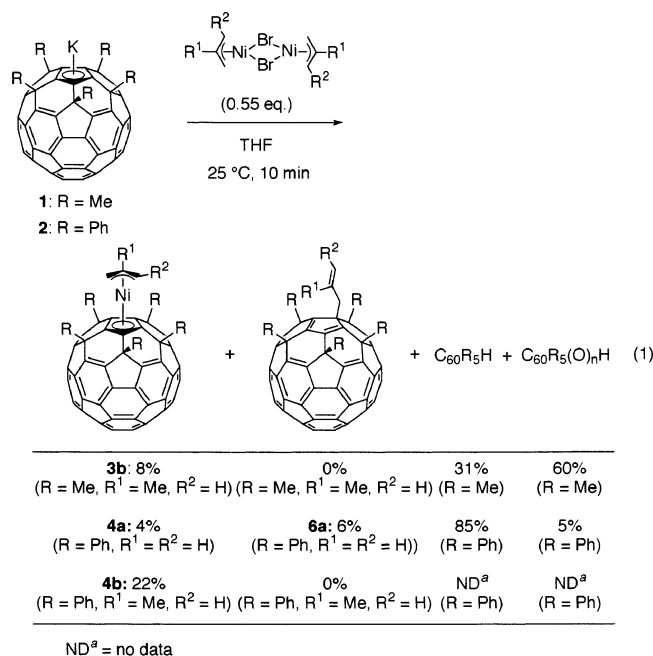
(13) Toganoh, M.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2003**, *125*, 13974.

PhFCp transition-metal complexes, very likely because of steric congestion imposed by the five phenyl groups surrounding the cyclopentadienide moiety. This observation in turn suggested us that the PhFCp ligand may act to stabilize the otherwise unstable transition-metal complex by steric protection. In this article, we report the first synthesis of PhFCp transition-metal complexes (as well as MeFCp complexes) for the group 10 triad and show that the PhFCp ligand allows the preparation of the first stable nickel π -allyl complex, which is stable to heat, water, and molecular oxygen at high temperature (80 °C). Palladium and platinum complexes, Pd(η^5 -C₆₀R₅)(η^3 -allylic) (allylic = allyl, methallyl, crotyl; R = Me, Ph) and Pt(η^5 -C₆₀R₅)(η^3 -methallyl) (R = Me, Ph), have also been synthesized and provide clues in understanding the origin of the stabilization effects of the C₆₀-Ph₅ group.

Results and Discussion

Synthesis of the Nickel-RFCp Complexes. The parent π -allyl nickel complex Ni(η^5 -Cp)(η^3 -allyl) is a sensitive compound; it can be handled at ambient temperature and is stable to water but instantly decomposes upon exposure to air, as confirmed by our own hand.¹⁴ We therefore synthesized the π -allyl nickel complexes to see if the FCp ligand can stabilize them. Because of the electronegative fullerene core, the FCp anion is thermodynamically more stable than the C₅H₅ anion.¹⁵ Between MeFCp and PhFCp, the latter is markedly more congested sterically (vide infra). We thus synthesized the π -allyl nickel complexes of the MeFCp and PhFCp ligands.

Metal exchange starting with potassium complexes afforded the desired complexes. The reactions of K(η^5 -RFCp) (**1**,^{7c} R = Me; **2**,^{7a} R = Ph) with [Ni(allylic)Br]₂ (allylic = allyl, methallyl)¹⁶ provided the desired nickel complexes Ni(η^5 -RFCp)(η^3 -allylic) (**3b**, allylic = methallyl, R = Me; **4a**, allylic = allyl, R = Ph; **4b**, allylic = methallyl, R = Ph) (eq 1). After purification by prepara-



tive HPLC separation, complexes **3b** and **4a,b** were obtained in 4–22% isolated yield. Attempted synthesis

of Ni(η^5 -MeFCp)(η^3 -allyl) resulted in exclusive formation of the allylated product C₆₀Me₅(CH₂CH=CH₂) (**5a**) in 22% yield. In the synthesis of **4a**, the allyl compound C₆₀Ph₅(CH₂CH=CH₂) (**6a**) was also obtained as a side product in 6% yield. The remainder of the material balance was largely the starting material C₆₀Ph₅H (85%) and its oxidation products¹⁷ (5%) that were formed during workup. Once formed, **4a** does not decompose to give **6a** upon heating. A plausible possibility is that the allylic compounds **5a**, **6a**, and **5b** were formed in situ by the nucleophilic attack of anions MeFCp[−] and PhFCp[−] at the allylic palladium or platinum species.¹⁸

Structure assignment was achieved by the standard physical methods. High-resolution APCI-TOF-MS(+) data were consistent with the assigned structures. The ¹H and ¹³C NMR measurements of nickel complexes **3b** and **4a,b** indicated that the FCp moieties have C_{5v} symmetry. For instance, the ¹³C NMR spectrum displayed only eight signals due to the C_{5v}-symmetric fullerene skeleton: the cyclopentadienyl moiety (δ 111.88), the sp³ fullerene carbon atom (δ 51.01), the sp² carbon atom next to the sp³ carbon (δ 154.19), and five other types of fullerene sp² carbon atoms (δ 143.30, 145.05, 146.39, 147.55, and 148.29), together with a methyl group signal (δ 30.08) and signals due to the methallyl ligand (δ 29.79 (CH₃), 44.20 (CH₂), and 100.51 (center carbon)). Therefore, the rotation of the FCp moiety around the Ni-FCp axis and the five addends on the fullerene sp³ carbon atoms is faster than the NMR relaxation time.

All FCp nickel complexes **3b** and **4a,b** were found to be far more stable than the parent π -allyl complex Ni(η^5 -Cp)(η^3 -allyl), which decomposes in 1 min upon exposure to air. For instance, the methallyl MeFCp complex **3b** in toluene decomposes very slowly in air at 25 °C, leaving 30% of the material even after 5 days. *The PhFCp complexes are far more stable: heating a stirred toluene solution of the complexes 4a,b in air at 80 °C for 15 h resulted in quantitative recovery.*

Synthesis of the Palladium and Platinum Complexes. While the nickel complexes did not give crystals suitable for crystallographic analysis, the corresponding palladium complexes produced single crystals and hence gave us information on their molecular structure and the origin of the stabilization. Electrochemical measurements also afforded data relevant to the properties of the FCp ligands. Platinum complexes were also synthesized, albeit in low yield.

(14) In our reexamination of the synthesis and properties of Ni(η^3 -allyl)(η^5 -Cp), this complex is stable to water but reacts rapidly with air to give a pale yellow solid. Since the molecular ion peak corresponding to the molecular weight of allylcyclopentadiene was detected by GC-MS measurements, we speculate that Ni(η^3 -allyl)(η^5 -Cp) decomposes via the oxidation of the nickel followed by reductive elimination of allylcyclopentadiene.

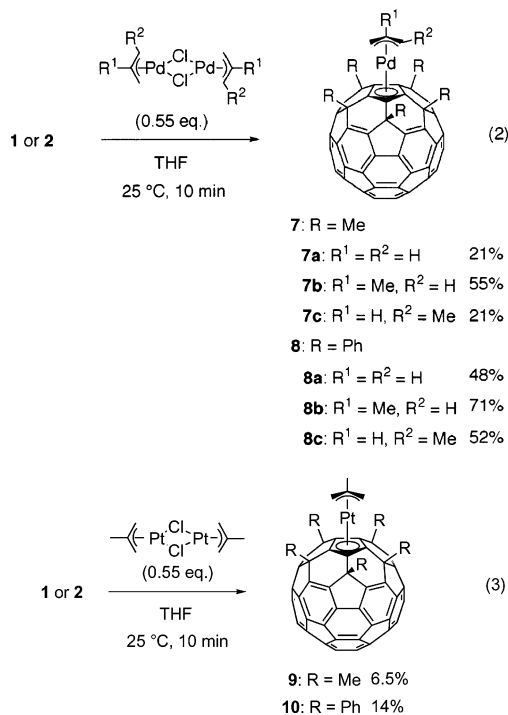
(15) (a) Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E.; Zhou, S.-Q.; Chu, B. *Chem. Lett.* **2000**, 1098. (b) Zhou, S.-Q.; Burger, C.; Chu, B.; Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E. *Science* **2001**, *291*, 1944.

(16) π -Allyl nickel halide: (a) U. S. Patent 3 422 128, Jan 14th, 1969. (b) German Published Patent Application 1 194 417, Aug 10th, 1963 (Studiengesellschaft Kohle).

(17) (a) Avent, A. G.; Birkett, P. R.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Chem. Commun.* **1997**, 1579. (b) Al-Matar, M.; Hitchcock, P. B.; Avent, A. G.; Taylor, R. *Chem. Commun.* **2000**, 1071.

(18) Davies, J. A. Palladium–Carbon π -Bonded Complexes. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 9, p 291.

The syntheses followed those of the nickel complexes. The palladium and platinum allyl and methallyl complexes Pd(η^5 -RFCp)(η^3 -allylic) (**7a**, allylic = allyl, R = Me; **7b**, allylic = methallyl, R = Me; **7c**, allylic = crotyl, R = Me; **8a**, allylic = allyl, R = Ph; **8b**, allylic = methallyl, R = Ph; **8c**, allylic = crotyl, R = Ph) and Pt-(η^5 -RFCp)(η^3 -methallyl) (**9**, R = Me; **10**, R = Ph) were synthesized by transmetalation of the potassium salt **1** or **2** with [Pd(η^3 -allylic)Cl]₂ (allylic = allyl, methallyl, crotyl)¹⁹ or [Pt(η^3 -methallyl)Cl]₂²⁰ (eqs 2 and 3). After



purification by preparative HPLC, the palladium complexes **7a–c** and **8a–c** and the platinum complexes **9** and **10** were obtained in 21–71% (palladium complexes) and 6.5–14% (platinum complexes) isolated yield, respectively.

As in the synthesis of the nickel complexes, the synthesis of the palladium and platinum complexes also produced allylated and methallylated side products, C₆₀Me₅(CH₂CH=CH₂) (**5a**), C₆₀Ph₅(CH₂CH=CH₂) (**6a**), and C₆₀Me₅(CH₂C(Me)=CH₂) (**5b**), in 8–10% yield. Like the nickel complexes **3** and **4**, the palladium complexes **7a** and **8a** and platinum complex **9** did not decompose into allylic compounds **5a**, **6a**, and C₆₀Me₅(CH₂C(Me)=CH₂) (**5b**) upon heating.

Identification of these palladium and platinum complexes was achieved by high-resolution APCI-TOF-MS(+) and ¹H and ¹³C NMR measurements. The ¹H NMR spectra of the platinum complexes **9** and **10** exhibited platinum–hydrogen spin–spin coupling (**9**, *J*_{Pt–H(Me)} = 27.2, *J*_{Pt–H(syn)} = 111.6, *J*_{Pt–H(anti)} = 63.6 Hz; **10**, *J*_{Pt–H(Me)} = 32.1, *J*_{Pt–H(syn)} = 117.8, *J*_{Pt–H(anti)} = 64.6 Hz). The magnitude of the coupling agrees well with that in Pt-(η^5 -Cp)(η^3 -methallyl)²¹ (*J* = 34, 111, 61 Hz). The allylic

Table 1. Comparison of ¹H NMR Chemical Shifts (ppm) between π -Allylic Ligands of Palladium Complexes **7a–c** and **8a–c**

| | H _a | H _b | H _c | H _d | H _e | Me _c | Me _d |
|--|----------------|----------------|----------------|--------------------|--------------------|-----------------|-----------------|
| 7a | 2.99 | 4.32 | 5.51 | (=H _b) | (=H _a) | | |
| 7b | 2.94 | 4.25 | | (=H _b) | (=H _a) | 2.36 | |
| 7c | 2.81 | 4.10 | 5.41 | | | | 2.02 |
| 8a | 2.09 | 3.08 | 4.70 | (=H _b) | (=H _a) | | |
| 8b | 1.95 | 2.99 | | (=H _b) | (=H _a) | 1.63 | |
| 8c | 1.73 | 2.67 | 4.66 | | | 3.08 | 0.51 |
| Pd(η^3 -allyl)(η^5 -C ₅ Me ₅) | 1.91 | 2.96 | 4.75 | | | | |
| Pd(η^3 -allyl)(η^5 -C ₅ Ph ₅) | 2.66 | 3.65 | 5.30 | | | | |

protons in the Pd–PhFCp complexes **8a–c** were observed at higher magnetic field (δ 2.09, 3.08, and 4.70) than were the Pd–C₅Ph₅ protons (δ 2.66, 3.65, and 5.30 ppm) (Table 1).^{19d} The upfield shift is caused by the proximity of the five phenyl groups surrounding the π -allylic palladium moiety, which will be discussed later regarding the crystal structures of **8a–c** (Figure 2). This upfield shift stands in contrast to the downfield shift upon going from the C₅Me₅ to the C₅Ph₅ compound in a simple Cp series; namely, the proton signals of the π -allylic palladium moiety of the C₅Ph₅ palladium complex Pd(η^5 -C₅Ph₅)(η^3 -allyl)^{19d} appears at lower magnetic field (δ 1.91, 2.96, and 4.75) than those of the C₅Me₅ palladium complex Pd(η^5 -C₅Me₅)(η^3 -allyl)^{19c} (Table 1).

X-ray Crystal Structural Analysis. Dark red single crystals of palladium complexes **7a,b** and **8a–c** suitable for X-ray crystallographic analysis were obtained by recrystallization from CS₂/EtOH, and the structures are shown in Figures 1 and 2. The FCp ligands coordinate to the palladium atom in an η^5 fashion to make a sandwich structure. The hydrogen atoms on the π -allylic ligand in the palladium–PhFCp complexes **8a–c** are located in the space surrounded by five phenyl groups. This spatial arrangement accounts for the upfield shift of the allylic protons of the palladium–PhFCp complexes **8a–c** discussed above. The average bond lengths of the five Pd–C(FCp) bonds in the palladium–MeFCp (**7a,b**) and –PhFCp complexes (**8a–c**) (2.34 Å for **7a**, 2.36 Å for **7b**, 2.37 Å for **8a**, 2.37 Å for **8b**, and 2.40 Å for **8c**) are slightly longer than that of the simple Cp complex Pd(η^5 -Cp)(η^3 -allyl)²² (2.26 Å) (Table 2). The bond lengths of the three Pd–C(π -allylic) bonds in complexes **7a,b** and **8a–c** (2.15, 2.09, 2.18 Å for **7a**; 2.13, 2.11, 2.13 Å for **7b**; 2.13, 2.08, 2.15 Å for **8a**; 2.13, 2.13, 2.14 Å for **8b**; 2.18, 2.10, 2.16 Å for **8c**) are also slightly longer than those of Pd(η^5 -Cp)(η^3 -allyl)²² (2.10, 2.04, 2.07 Å) (Table 2). All bond lengths in the palladium–MeFCp and –PhFCp series are identical with each other within the standard deviation, indicating that there is little steric hindrance between the allyl moiety and the RFCp ligand. In agreement with this conclusion, the closest C–H and H–H bond distances in the Pd–PhFCp complexes are 2.89–3.28 Å (between carbon atoms of the five phenyl groups and the hydrogen atoms of the methallyl ligand, in **8b**) and 2.43–3.04 Å (between

(19) (a) Shaw, B. L. *Proc. Chem. Soc.* **1960**, 247. (b) Parker, G.; Werner, H. *Helv. Chim. Acta* **1973**, *56*, 2819. (c) Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H.-J.; Kruger, C. *Organometallics* **1983**, *2*, 1369. (d) Powell, J.; Dowling, N. I. *Organometallics* **1983**, *2*, 1742.

(20) Mabbott, D. J.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 294.

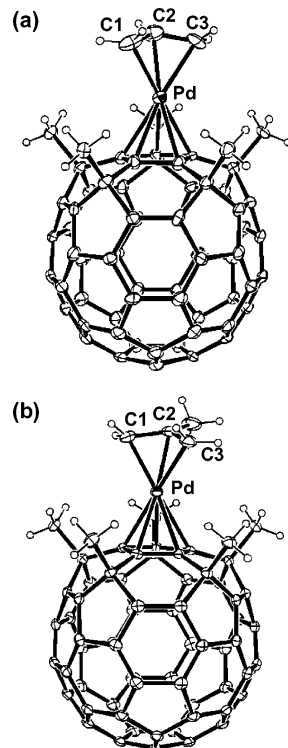
(21) Mann, B. E.; Shaw, B. L.; Shaw, G. *J. Chem. Soc. A* **1971**, 3536.

(22) Minasyants M. K.; Struchkov, Y. T. *Zh. Strukt. Khim.* **1968**, *9*, 481.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Palladium Complexes **7a**, **b** and **8a–c**

| | 7a | 7b | 8a | 8b | 8c | Pd(π -allyl)Cp |
|----------------------------------|-----------|-----------|-----------|-----------|-----------|---------------------|
| Pd–C(FCp) (av) | 2.337(9) | 2.357(3) | 2.370(3) | 2.367(5) | 2.398(6) | 2.26 |
| Pd–C1 | 2.153(12) | 2.131(4) | 2.134(5) | 2.126(6) | 2.18(2) | 2.10 |
| Pd–C2 | 2.090(12) | 2.105(4) | 2.076(5) | 2.130(7) | 2.10(2) | 2.04 |
| Pd–C3 | 2.179(12) | 2.131(5) | 2.148(5) | 2.143(8) | 2.16(2) | 2.07 |
| fullerene angle sum ^a | 313.38 | 312.98 | 312.66 | 313.68 | 312.56 | |

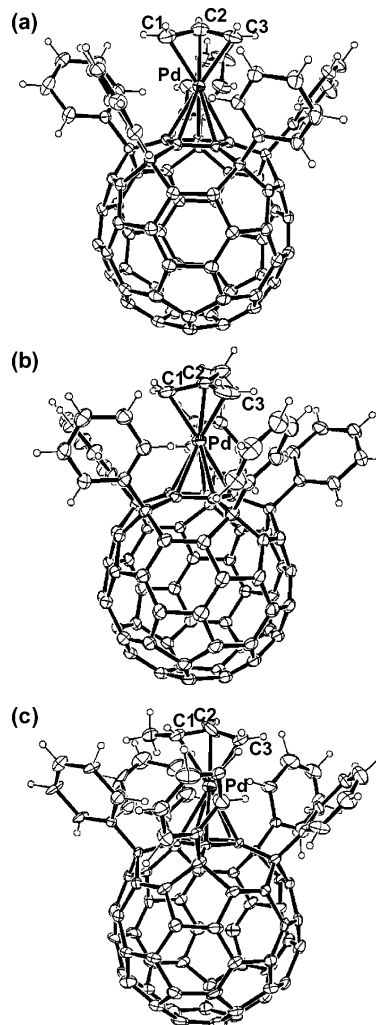
^a Sum of three angles around the fullerene sp³ carbon atoms, within the fullerene skeleton.

**Figure 1.** Molecular structures of the Pd–MeFCp complexes with 30% probability level ellipsoids: (a) **7a**·CS₂; (b) **7b**·1.5CS₂. The solvent molecules in the unit cell are omitted for clarity.

hydrogen atoms of the five phenyl groups and those of the methallyl ligand, in **8b**), respectively, and these distances are longer than the van der Waals contacts (H–C = 2.90 Å; H–H = 2.40 Å).²³

Electrochemical Investigations. Cyclic voltammetry (CV) gives useful information on the electronic properties of metal complexes and provided insights into the properties of the PhFCp metal complexes. The redox behavior of the π -allyl palladium complexes **7a** and **8a** is shown in Figure 3 and Table 3, and the data are compared with those of Fe(η^5 -Cp)(η^5 -MeFCp),⁹ Ru(η^5 -MeFCp)(CH₃)(CO)₂,¹⁰ and Rh(η^5 -MeFCp)(CO)₂.¹²

Scanning between 0.82 and –2.87 V (vs Fc/Fc⁺, scan rate 100 mV/s) showed that the MeFCp complex **7a** is stable upon one-electron reduction (Figure 3a) but the PhFCp complex **8a** partially decomposes upon one-electron reduction (Figure 3b). The reduction potentials of **7a** and **8a** are comparable to those of Fe(η^5 -MeFCp)(η^5 -Cp),⁹ Ru(η^5 -MeFCp)(CH₃)(CO)₂,¹⁰ Rh(η^5 -MeFCp)(CO)₂,¹² and C₆₀Ph₅H.²⁴ We therefore consider that the reduction puts the electron into the fullerene moiety.

**Figure 2.** Molecular structures of the Pd–PhFCp complexes with 30% probability level ellipsoids: (a) **8a**·2.5CS₂; (b) **8b**·0.25CS₂; (c) **8c**·2CHCl₃. The solvent molecules in the unit cell are omitted for clarity.

The electron-withdrawing effect of the five phenyl groups makes the reduction of the PhFCp complex **8a** ($E_{1/2}^{\text{red1}} = -1.40$ V) easier than that of the MeFCp complex **7a** ($E_{1/2}^{\text{red1}} = -1.47$ V). This electron-deficient nature of the PhFCp complex accounts for the higher stability of the PhFCp nickel complex toward oxidation as compared to the MeFCp complex and also as compared to the simple Cp complexes.

The analysis of the CV data led us to speculate on the reactions taking place during the reduction/oxidation process (Figure 3b). In the course of the one-electron reductions of **8a**, new species formed together with the reduced complex **8a**^{•–}. In view of our previous work,²⁴ we consider the new species to be the anion PhFCp[–]; hence, the Pd–PhFCp bond was cleaved in the reduction processes. The result per se is nonproductive; nonethe-

(23) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960.

(24) Iikura, H.; Mori, S.; Sawamura, M.; Nakamura, E. *J. Org. Chem.* **1997**, *62*, 7912.

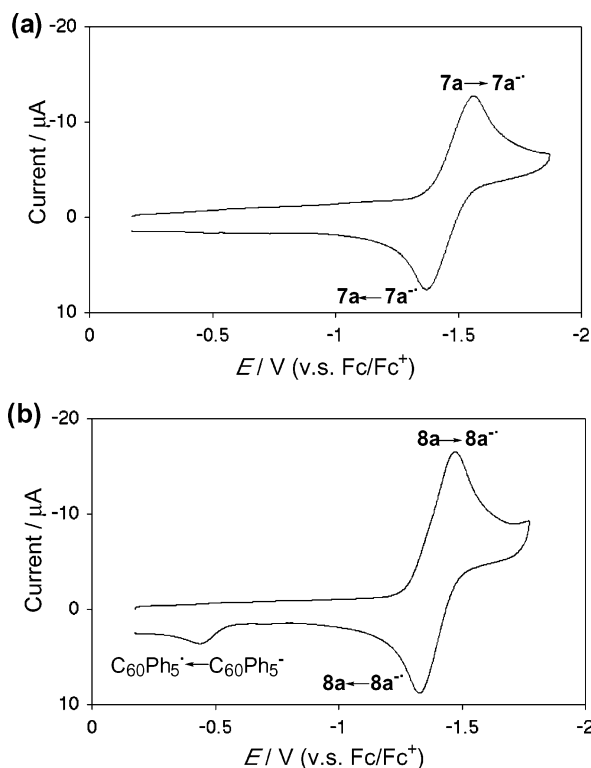


Figure 3. Cyclic voltammograms of the palladium–RFCp π -allyl complexes: (a) reversible one-electron reduction of **7a**; (b) irreversible one-electron reduction of **8a**. Both measurements were carried out in a 1.0 mM THF solution containing 100 mM [ⁿBu₄N][ClO₄] as a supporting electrolyte.

Table 3. Reduction Potentials for Palladium Complexes and Fullerene Derivatives^a

| | $E_{1/2}^{\text{red}}(1)$ (V) | $E_{1/2}^{\text{red}}(2)$ (V) |
|--|-------------------------------|-------------------------------|
| Pd(η^5 -MeFCp)(η^3 -allyl) (7a) | -1.47 | -2.06 ^b |
| Pd(η^5 -PhFCp)(η^3 -allyl) (8a) | -1.40 | -1.99 ^b |
| Fe(η^5 -MeFCp)(η^5 -Cp) ^c | -1.46 | -2.06 ^d |
| Ru(η^5 -MeFCp)(η^5 -Cp) ^e | -1.43 | -2.01 |
| Ru(η^5 -MeFCp)(CH ₃)(CO) ₂ ^f | -1.34 | -1.94 |
| Rh(η^5 -MeFCp)(CO) ₂ ^g | -1.35 | -1.94 |
| C ₆₀ Me ₅ H ^e | -1.48 | -2.07 |
| C ₆₀ Ph ₅ H ^h | -1.38 | -1.98 |

^a In V vs ferrocene/ferrocenium couple. 25 °C. ^b Irreversible reduction. ^c Reference 9. ^d Peak top potential. ^e Reference 11. ^f Reference 10. ^g Reference 12. ^h Reference 24.

less, it indicates that the electron, once supplied to the fullerene core, moves to the metal center through the cyclopentadienide moiety, suggesting the possibility of controlling the reactivity of the metal by manipulation of the fullerene moiety.

Conclusion: Kinetic and Thermodynamic Stabilization by the PhFCp Ligand. The PhFCp allyl nickel complexes Ni(η^5 -PhFCp)(η^3 -allyl) (**4a**) and Ni(η^5 -PhFCp)(η^3 -methallyl) (**4b**) are stable upon exposure to air, even at 80 °C for 12 h, while the parent nickel Cp allyl complexes instantly decompose in air at room temperature. We ascribe the high stability of the PhFCp complexes first to the steric shielding effect of the phenyl groups. To enhance such “kinetic” stability, a bulkier aryl group such as a biphenyl group²⁵ would be useful. “Thermodynamic” stabilization may also play a role:

(25) Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, 419, 702.

thus, the electron-deficient PhFCp complex is more stable toward molecular oxygen than the MeFCp complex and is much more stable than the simplex Cp complexes.

One may recall that a highly substituted version of the hydrotris(pyrazolyl)borate (Tp) ligand^{5,26–28} can significantly enhance the stability of transition-metal complexes^{29,30} and that the RFCp ligand can be modified in various ways: the R group can be either electron-withdrawing or donating, can be bulky or relatively less sterically hindering,³¹ may bear water-soluble groups such as sugar,³² and may be a part of a mesogenic structure.²⁵ We therefore expect that a variety of new possibilities for the control of the reactivities of metal centers will become available on the basis of the RFCp ligand systems.

Experimental Section

General Procedures. All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk techniques. THF was distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation. C₆₀Me₅H and C₆₀Ph₅H were prepared according to the literature.⁷ A THF solution of ^tBuOK was purchased from Sigma-Aldrich Co. and used as received. The complexes [Ni(η^3 -allyl)Br]₂,^{16a} [Ni(η^3 -methallyl)Br]₂,^{16b} [Pd(η^3 -allyl)Cl]₂,¹⁹ [Pd(η^3 -methallyl)Cl]₂,¹⁹ [Pd(η^3 -crotyl)Cl]₂,¹⁹ and [Pt(η^3 -methallyl)Cl]₂²⁰ were prepared as reported in the literature. Preparative HPLC separations were performed by use of a Buckyprep column (Nacalai Tesque Co., 20 mm × 250 mm). The ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded using a JEOL EX-400 spectrometer. Proton chemical shifts are reported relative to Me₄Si (CDCl₃) at δ 0.00 ppm or residual solvent signals (CDCl₃ at δ 7.26 ppm; THF-*d*₈ at δ 1.73 and 3.58 ppm). Carbon chemical shifts are reported relative to CDCl₃ at δ 77.00 ppm or THF-*d*₈ at δ 25.20 and 67.40 ppm. Other spectra were recorded on the following instruments: IR, JASCO IR-420 and ReactIR 1000; UV/vis spectra, Hitachi U3500 and Shimadzu SPD-6A; mass spectra, Shimadzu LCMS-QP8000, JEOL JMS-T100LC, and JEOL JMS-GCMATE II. Elemental analyses were performed at the organic elemental analysis laboratory in this department.

Preparation of Ni(η^5 -MeFCp)(η^3 -methallyl) (3b**).** To a suspension of C₆₀Me₅H (50.0 mg, 62.7 μ mol) in THF (5.0 mL) was added a solution of ^tBuOK (1.0 M, 69.0 μ L, 69.0 μ mol) in THF. To the resulting dark reddish orange solution was added [Ni(η^3 -methallyl)Br]₂ (13.4 mg, 34.5 μ mol). The reaction mixture was stirred at 25 °C for 10 min before being quenched by addition of saturated aqueous NH₄Cl (1.0 mL). The mixture was diluted with toluene and washed with water. The organic layer was dried over MgSO₄ and was concentrated under reduced pressure. Preparative HPLC separations (eluent 7/3 toluene/2-propanol) afforded **3b** (4.0 mg, 7.0% yield) as dark red fine crystals. ¹H NMR (400 MHz, CDCl₃): δ 2.29 (s, 3H), 2.30 (s, 15H), 2.54 (s, 2H), 3.61 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 29.79 (1C), 30.08 (5C), 44.20 (2C), 51.01 (5C), 100.51 (1C), 111.88 (5C), 143.30 (10C), 145.05 (10C), 146.39

(26) (a) Akita, M.; Shirasawa, N.; Hikichi, S.; Moro-oka, Y. *Chem. Commun.* **1998**, 973. (b) Shirasawa, N.; Nguyet, T. T.; Hikichi, S.; Moro-oka, Y.; Akita, M. *Organometallics* **2001**, 20, 3582.

(27) Kisko, J. L.; Hascall, T.; Parkin, G. *J. Am. Chem. Soc.* **1998**, 120, 10561.

(28) Jewson, J. D.; Liable-Sands, L. M.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1999**, 18, 300.

(29) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, 34, 115.

(30) Akita, M.; Hikichi, S.; Moro-oka, Y. *J. Synth. Org. Chem., Jpn.* **1999**, 57, 67.

(31) Matsuo, Y.; Muramatsu, A.; Hamasaki, R.; Mizoshita, N.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, 126, 432.

(32) Isobe, H.; Mashima, H.; Yorimitsu, H.; Nakamura, E. *Org. Lett.* **2003**, 5, 4461.

(5C), 147.55 (10C), 148.29 (5C), 154.19 (10C). IR (powder, cm^{-1}): ν 2959 (m), 2918 (m), 2854 (m), 1723 (m), 1441 (s), 1368 (m), 1286 (m), 1264 (m), 1236 (w), 1213 (w), 1200 (w), 1156 (w), 1115 (w), 1071 (w), 1018 (w), 902 (m), 802 (m), 752 (s), 728 (s), 685 (s), 666 (m), 658 (m). UV-vis (7/3 toluene/2-propanol, nm): λ_{max} 286, 348 (shoulder), 395, 480 (shoulder). HR-APCI-MS(−) (m/z): found, 908.1081; calcd for **3b**, 908.1075.

Preparation of Ni(η^5 -PhFCp)(η^3 -allyl) (4a**).** Complex **4a** was synthesized as for **3b**, using the following compounds: $\text{C}_{60}\text{Ph}_5\text{H}$ (50.0 mg, 45.2 μmol), BuOK (1.0 M, 49.7 μL , 49.7 μmol) in THF, $[\text{Ni}(\eta^3\text{-methallyl})\text{Br}]_2$ (8.93 mg, 24.8 μmol), and THF (1.0 mL). Yield: 2.2 mg (4.0%). ^1H NMR (400 MHz, CDCl_3): δ 1.18 (d, $^3J = 11.8$ Hz, 2H), 2.27 (d, $^3J = 6.4$ Hz, 2H), 4.99 (tt, $^3J = 11.8$ Hz, $^3J = 6.4$ Hz, 1H), 7.19–7.23 (m, 15H), 7.71 (d, $^3J = 7.4$ Hz, 10H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 51.00 (2C), 58.74 (5C), 98.46 (1C), 112.71 (5C), 127.48 (5C), 127.96 (10C), 128.40 (10C), 142.69 (5C), 143.55 (10C), 145.27 (10C), 146.95 (5C), 147.89 (10C), 148.74 (5C), 152.30 (10C). UV-vis (7/3 toluene/2-propanol, nm): λ_{max} 287, 355 (shoulder), 396, 470 (shoulder). HR-APCI-MS(−) (m/z): found, 1204.1628; calcd for **4a**, 1204.1701.

The reaction also gave the allylated pentaphenyl[60]-fullerene **6a** (2.2 mg, 6.0% yield) as a side product. ^1H NMR (400 MHz, CDCl_3): δ 2.24 (d, $^3J = 6.8$ Hz, 2H), 4.64 (dd, $^3J = 19.2$ Hz, $^3J = 2.0$ Hz, 1H), 5.10 (dd, $^3J = 12.4$ Hz, $^3J = 2.0$ Hz, 1H), 5.96 (ddt, $^3J = 19.2$ Hz, $^3J = 12.4$ Hz, $^3J = 6.8$ Hz, 1H), 7.16–7.19 (m, 4H), 7.30–7.43 (m, 13H), 7.75–7.78 (m, 4H), 7.87–7.90 (m, 4H). ^1H NMR (400 MHz, 1/3 $\text{CDCl}_3/\text{CS}_2$): δ 2.18 (d, $^3J = 6.8$ Hz, 2H), 4.58 (d, $^3J = 17.2$ Hz, 2H), 5.02 (d, $^3J = 10.0$ Hz, 2H), 5.89 (ddt, $^3J = 17.2$ Hz, $^3J = 10.0$ Hz, $^3J = 6.8$ Hz, 1H), 7.09–7.11 (m, 4H), 7.22–7.32 (m, 13H), 7.67–7.69 (m, 4H), 7.77–7.79 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 1/3 $\text{CDCl}_3/\text{CS}_2$): δ 43.81 (1C), 58.26 (2C), 60.80 (1C), 62.86 (1C), 64.81 (2C), 118.91 (1C), 126.77 (1C), 127.34 (2C), 127.47 (2C), 127.73 (2C), 127.85 (4C), 128.05 (4C), 128.41 (4C), 128.52 (4C), 130.23 (2C), 133.56 (2C), 137.97 (2C), 139.40 (1C), 142.01 (1C), 142.36 (2C), 143.13 (2C), 143.30 (2C), 143.50 (2C), 143.68 (2C), 143.76 (2C), 143.83 (2C), 143.95 (2C), 144.08 (2C), 144.19 (2C), 144.89 (2C), 145.01 (2C), 146.68 (1C), 146.87 (2C), 146.92 (2C), 147.06 (2C), 147.43 (1C), 147.66 (2C), 147.80 (2C), 147.89 (2C), 148.05 (2C), 148.19 (2C), 148.32 (2C), 148.39 (2C), 150.85 (2C), 152.48 (2C), 155.85 (2C), 156.25 (2C). IR (powder, cm^{-1}): ν 3056 (w), 3023 (w), 2956 (w), 2920 (m), 2851 (m), 1961 (w), 1943 (w), 1724 (brm), 1597 (m), 1491 (m), 1462 (m), 1445 (m), 1419 (w), 1376 (w), 1288 (w), 1260 (m), 1237 (w), 1203 (w), 1183 (w), 1156 (w), 1069 (m), 1029 (s), 1003 (m), 910 (m), 896 (w), 837 (w), 799 (m), 758 (m), 742 (m), 733 (m), 693 (s), 683 (m), 671 (m). UV-vis (1.0×10^{-5} mol L^{-1} in CH_2Cl_2 ; λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 260 (81 800, shoulder), 272 (75 100, shoulder), 354 (22 300, shoulder), 395 (11 800, shoulder), 474 (4310, shoulder). APCI-MS(\pm) (m/z): = 1147 ($[\text{M} + \text{H}]^+$), 1146 (M^-). Anal. Calcd for **6a**·0.5 CS_2 : C, 94.74; H, 2.55. Found: C, 94.60; H, 3.02.

Preparation of Ni(η^5 -PhFCp)(η^3 -methallyl) (4b**).** Complex **4b** was synthesized as for **3b**, using the following compounds: $\text{C}_{60}\text{Ph}_5\text{H}$ (10.0 mg, 9.03 μmol), BuOK (1.0 M, 10.0 μL , 10.0 μmol) in THF, $[\text{Ni}(\eta^3\text{-methallyl})\text{Br}]_2$ (1.92 mg, 4.97 μmol), and THF (1.0 mL). Yield: 2.4 mg (22%). ^1H NMR (400 MHz, CDCl_3): δ 1.12 (s, 2H), 1.59 (s, 3H), 2.17 (s, 2H), 7.25 (t, $^3J = 7.6$ Hz, 10H), 7.29 (d, $^3J = 7.6$ Hz, 5H), 7.73 (d, $^3J = 7.6$ Hz, 10H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 29.79 (1C), 50.62 (2C), 58.96 (5C), 100.87 (1C), 112.69 (5C), 127.34 (5C), 127.91 (10C), 128.53 (10C), 142.69 (5C), 143.40 (10C), 145.09 (10C), 146.82 (5C), 147.76 (10C), 148.58 (5C), 152.12 (10C). IR (powder, cm^{-1}): ν 2960 (m), 2922 (s), 2851 (m), 1720 (m), 1599 (m), 1492 (m), 1459 (m), 1445 (m), 1418 (w), 1285 (m), 1261 (s), 1238 (m), 1201 (m), 1155 (m), 1105 (m), 1091 (m), 1072 (m), 1030 (s), 1018 (s), 959 (m), 832 (m), 798 (s), 761 (m), 734 (s), 711 (m), 697 (s), 668 (m). UV-vis (7/3 toluene/2-propanol, nm) λ_{max} 285, 334 (shoulder), 356 (shoulder), 393, 475 (shoul-

der). HR-APCI-MS(−) (m/z): found, 1218.1968; calcd for **4b**, 1218.1858.

Preparation of Pd(η^5 -MeFCp)(η^3 -allyl) (7a**).** Complex **7a** was synthesized as for **3b**, using the following compounds: $\text{C}_{60}\text{Me}_5\text{H}$ (100 mg, 125 μmol), BuOK (1.0 M, 138 μL , 138 μmol) in THF, $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}]_2$ (25.2 mg, 68.9 μmol), and THF (10.0 mL). Yield: 25 mg (21%). ^1H NMR (400 MHz, CDCl_3): δ 2.32 (s, 15H), 2.99 (d, $^3J = 11.2$ Hz, 2H), 4.32 (d, $^3J = 6.4$ Hz, 2H), 5.51 (tt, $^3J = 11.2$ Hz, $^3J = 6.4$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 32.13 (5C), 47.90 (2C), 51.02 (5C), 95.89 (1C), 119.13 (5C), 143.32 (10C), 145.19 (10C), 146.30 (5C), 147.47 (10C), 148.30 (5C), 154.03 (10C). IR (powder, cm^{-1}): ν 2957 (m), 2913 (m), 2853 (w), 1603 (w), 1579 (w), 1548 (w), 1514 (w), 1494 (m), 1454 (m), 1439 (s), 1416 (m), 1366 (m), 1286 (w), 1265 (m), 1236 (m), 1219 (w), 1200 (m), 1178 (w), 1155 (m), 1136 (m), 1111 (m), 1080 (w), 1009 (m), 951 (w), 904 (m), 728 (s), 695 (m), 684 (s), 657 (m). UV-vis (1.0×10^{-5} mol L^{-1} in CH_2Cl_2 ; λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 273 (78 700), 339 (35 300), 356 (30 400, shoulder), 395 (13 100, shoulder), 472 (3430, shoulder). APCI-MS(+) (m/z): 942 (M^+). Anal. Calcd for **7a**·0.5 CS_2 : C, 83.83; H, 2.05. Found: C, 83.35; H, 2.23.

The reaction also gave the allylated pentamethyl[60]-fullerene **5a** (8.6 mg, 8.2% yield) as a side product. ^1H NMR (400 MHz, CDCl_3): δ 2.24 (s, 6H), 2.27 (s, 6H), 2.40 (s, 3H), 3.27 (d, $^3J = 7.2$ Hz, 2H), 5.27 (dd, $^3J = 16.0$ Hz, $^3J = 2.0$ Hz, 1H), 5.41 (dd, $^3J = 10.0$ Hz, $^3J = 2.0$ Hz, 1H), 6.19 (ddt, $^3J = 16.0$ Hz, $^3J = 10.0$ Hz, $^3J = 7.2$ Hz, 1H). ^1H NMR (400 MHz, 1/3 $\text{CDCl}_3/\text{CS}_2$): δ 2.28 (s, 6H), 2.30 (s, 6H), 2.43 (s, 3H), 3.29 (d, $^3J = 7.2$ Hz, 2H), 5.30 (dd, $^3J = 16.0$ Hz, $^3J = 2.0$ Hz, 1H), 5.41 (dd, $^3J = 10.0$ Hz, $^3J = 2.0$ Hz, 1H), 6.21 (ddt, $^3J = 16.0$ Hz, $^3J = 10.0$ Hz, $^3J = 7.2$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 1/3 $\text{CDCl}_3/\text{CS}_2$): δ 24.31 (2C), 27.16 (2C), 28.92 (1C), 40.02 (1C), 50.31 (2C), 52.40 (2C), 53.40 (1C), 61.80 (1C), 118.66 (1C), 131.48 (1C), 142.49 (2C), 142.98 (2C), 143.59 (2C), 143.61 (2C), 144.00 (2C), 144.04 (2C), 144.08 (2C), 144.39 (2C), 144.42 (2C), 145.05 (2C), 145.54 (2C), 146.25 (2C), 146.44 (2C), 146.46 (2C), 147.37 (2C), 147.49 (2C), 147.56 (1C), 147.65 (2C), 147.86 (2C), 147.97 (2C), 147.99 (1C), 148.06 (2C), 148.20 (2C), 148.91 (2C), 153.23 (2C), 154.34 (2C), 155.21 (2C), 157.30 (2C). IR (powder, cm^{-1}): ν 2957 (m), 2915 (m), 2855 (w), 1636 (w), 1603 (w), 1573 (w), 1545 (w), 1521 (w), 1494 (w), 1458 (m), 1439 (s), 1416 (m), 1370 (m), 1286 (m), 1266 (m), 1238 (m), 1200 (m), 1174 (w), 1160 (w), 1153 (w), 1142 (w), 1129 (m), 1105 (m), 1041 (w), 984 (m), 952 (w), 912 (s), 803 (m), 790 (m), 778 (w), 771 (m), 725 (s), 713 (m), 695 (m), 688 (s), 667 (m). UV-vis (1.0×10^{-5} mol L^{-1} in CH_2Cl_2 ; λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 255 (66 800, shoulder), 348 (21 900), 356 (20 600, shoulder), 396 (12 500), 476 (3450, shoulder). APCI-MS(+) (m/z): 837 ($[\text{M} + \text{H}]^+$). Anal. Calcd for **5a**·0.5 CS_2 : C, 94.03; H, 2.30. Found: C, 94.31; H, 2.75.

Preparation of Pd(η^5 -MeFCp)(η^3 -methallyl) (7b**).** Complex **7b** was synthesized as for **3b**, using the following compounds: $\text{C}_{60}\text{Me}_5\text{H}$ (100 mg, 125 μmol), BuOK (1.0 M, 138 μL , 138 μmol) in THF, $[\text{Pd}(\eta^3\text{-methallyl})\text{Cl}]_2$ (27.2 mg, 68.9 μmol), and THF (10.0 mL). Yield: 66.0 mg (55%). ^1H NMR (400 MHz, CDCl_3): δ 2.33 (s, 15H), 2.36 (s, 3H), 2.94 (s, 2H), 4.25 (s, 2H). ^1H NMR (400 MHz, $\text{THF}-d_6$): δ 2.38 (s, 15H), 2.46 (s, 3H), 3.05 (s, 2H), 4.39 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 24.52 (1C), 31.90 (5C), 49.17 (5C), 51.08 (2C), 113.41 (1C), 118.94 (5C), 143.31 (10C), 145.24 (10C), 146.29 (5C), 147.46 (10C), 148.31 (5C), 154.14 (10C). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{THF}-d_6$): δ 24.47 (1C), 32.11 (5C), 50.35 (2C), 52.24 (5C), 115.19 (1C), 119.89 (5C), 144.10 (10C), 146.31 (10C), 147.15 (5C), 148.28 (10C), 149.12 (5C), 155.51 (10C). IR (powder, cm^{-1}): ν 2956 (m), 2912 (m), 2852 (w), 1571 (w), 1547 (w), 1514 (w), 1494 (w), 1454 (m), 1440 (s), 1410 (m), 1378 (w), 1365 (m), 1285 (w), 1265 (m), 1230 (m), 1199 (m), 1155 (m), 1136 (m), 1111 (m), 1030 (w), 1020 (m), 986 (w), 951 (w), 923 (w), 830 (s), 806 (w), 789 (w), 767 (w), 726 (s), 692 (m), 685 (s), 669 (m), 657 (m). UV-vis (1.0×10^{-5} mol L^{-1} in CH_2Cl_2 ; λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 272 (97 300), 338 (44 500), 358 (34 700, shoulder),

391 (15 900), 473 (4220, shoulder). APCI-MS(+) (*m/z*): 956 (M⁺). Anal. Calcd for **7b**: C, 86.57; H, 2.32. Found: C, 86.80; H, 2.60.

Preparation of Pd(η^5 -MeFCp)(η^3 -crotyl) (7c**).** Complex **7c** was synthesized as for **3b**, using the following compounds: C₆₀Me₅H (100 mg, 125 μ mol), ^tBuOK (1.0 M, 138 μ L, 138 μ mol) in THF, [Pd(η^3 -crotyl)Cl]₂ (27.2 mg, 68.9 μ mol), and THF (10.0 mL). Yield: 25.6 mg (21%). ¹H NMR (400 MHz, CDCl₃): δ 2.02 (d, ³*J* = 6.0 Hz, 3H), 2.34 (s, 15H), 2.81 (d, ³*J* = 10.8 Hz, 1H), 4.06 (dq, ³*J* = 10.8 Hz, 1H), 4.10 (d, ³*J* = 6.4 Hz, 1H), 5.41 (ddd, ³*J* = 10.8 Hz, ³*J* = 10.8 Hz, ³*J* = 6.4 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 22.60 (1C), 31.75 (5C), 44.18 (1C), 51.26 (5C), 71.47 (1C), 97.39 (1C), 119.17 (5C), 143.28 (10C), 145.22 (10C), 146.28 (5C), 147.44 (10C), 148.29 (5C), 154.19 (10C). IR (powder, cm⁻¹): ν 2957 (m), 2914 (m), 2854 (w), 1454 (w), 1440 (s), 1417 (w), 1366 (m), 1285 (w), 1265 (m), 1236 (m), 1199 (m), 1156 (m), 1136 (m), 1111 (m), 1019 (m), 984 (w), 962 (w), 877 (w), 831 (w), 727 (m), 694 (w), 685 (s), 657 (m). UV-vis (1.0 \times 10⁻⁵ mol L⁻¹ in CH₂Cl₂; λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 258 (78 000, shoulder), 273 (71 800, shoulder), 348 (23 100, shoulder), 390 (13 800, shoulder), 471 (4590, shoulder). HR-APCI-MS(+) (*m/z*): found, 956.0753; calcd for **7c**, 956.0756.

Preparation of Pd(η^5 -PhFCp)(η^3 -allyl) (8a**).** Complex **8a** was synthesized as for **3b**, using the following compounds: C₆₀-Me₅H (100 mg, 90.3 μ mol), ^tBuOK (1.0 M, 99.3 μ L, 99.3 μ mol) in THF, [Pd(η^3 -crotyl)Cl]₂ (18.2 mg, 49.7 μ mol), and THF (10.0 mL). Yield: **8a**, 54.3 mg (48%); **6a**, 9.5 mg (9.2%). Data for **8a** are as follows. ¹H NMR (400 MHz, CDCl₃): δ 2.09 (d, ³*J* = 11.2 Hz, 2H), 3.08 (d, ³*J* = 6.4 Hz, 2H), 4.70 (tt, ³*J* = 11.2 Hz, ³*J* = 6.4 Hz, 1H), 7.16–7.20 (m, 15H), 7.77–7.79 (m, 10H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 57.64 (2C), 59.07 (5C), 100.13 (1C), 120.73 (5C), 127.26 (5C), 127.73 (10C), 128.19 (10C), 143.43 (10C), 143.96 (10C), 145.40 (10C), 146.71 (5C), 147.66 (5C), 148.62 (5C), 152.22 (10C). IR (powder, cm⁻¹): ν 3055 (m), 3027 (m), 2999 (w), 2921 (m), 2855 (m), 2350 (w), 2336 (w), 2216 (w), 2191 (w), 1959 (m), 1942 (m), 1887 (m), 1872 (m), 1798 (m), 1596 (s), 1589 (m), 1575 (m), 1491 (s), 1457 (s), 1444 (s), 1419 (m), 1378 (w), 1346 (w), 1332 (w), 1326 (w), 1284 (m), 1267 (m), 1237 (m), 1218 (m), 1200 (m), 1180 (m), 1156 (m), 1107 (m), 1071 (m), 1053 (m), 1030 (s), 1012 (m), 960 (s), 950 (w), 928 (w), 910 (m), 893 (m), 836 (m), 761 (m), 743 (m), 733 (m), 711 (m), 691 (s), 685 (s), 664 (m). UV-vis (1.0 \times 10⁻⁵ mol L⁻¹ in CH₂Cl₂; λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 260 (115 000), 280 (94 600, shoulder), 340 (43 400, shoulder), 356 (39 000, shoulder), 396 (18 200). APCI-MS(+) (*m/z*): 1252 (M⁺). Anal. Calcd for **8a**·0.5C₇H₈: C, 89.18; H, 2.64. Found: C, 89.28; H, 2.90.

Preparation of Pd(η^5 -PhFCp)(η^3 -methallyl) (8b**).** Complex **8b** was synthesized as for **3b**, using the following compounds: C₆₀Ph₅H (100 mg, 90.3 μ mol), ^tBuOK (1.0 M, 99.3 μ L, 99.3 μ mol) in THF, [Pd(η^3 -methallyl)Cl]₂ (19.6 mg, 49.7 μ mol), and THF (10.0 mL). Yield: 81.6 mg (71%). ¹H NMR (400 MHz, CDCl₃): δ 1.63 (s, 3H), 1.95 (s, 2H), 2.99 (s, 2H), 7.15–7.21 (m, 15H), 7.79–7.81 (m, 10H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 21.62 (1C), 57.82 (2C), 59.18 (5C), 116.07 (1C), 120.66 (5C), 127.19 (5C), 127.79 (10C), 128.26 (10C), 143.41 (10C), 144.10 (5C), 145.40 (10C), 146.70 (5C), 147.65 (10C), 148.60 (5C), 152.25 (10C). IR (powder, cm⁻¹): ν 3055 (m), 3023 (m), 3002 (w), 2916 (m), 2855 (m), 1958 (m), 1866 (m), 1805 (m), 1596 (m), 1493 (s), 1456 (m), 1445 (m), 1417 (m), 1377 (m), 1284 (m), 1265 (w), 1235 (m), 1202 (m), 1155 (m), 1108 (m), 1081 (w), 1072 (w), 1053 (w), 1031 (m), 1021 (m), 1003 (w), 983 (w), 959 (m), 911 (m), 894 (m), 831 (m), 822 (w), 788 (w), 781 (w), 760 (m), 751 (m), 742 (s), 711 (m), 693 (s), 684 (s), 664 (s). UV-vis (1.0 \times 10⁻⁵ mol L⁻¹ in CH₂Cl₂; λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 260 (83 400), 276 (73 400, shoulder), 340 (30 900), 358 (27 200, shoulder), 395 (12 800, shoulder). APCI-MS(+) (*m/z*): 1266 (M⁺). Anal. Calcd for **8b**·0.25C₅H₈: C, 87.98; H, 2.51. Found: C, 87.85; H, 2.72.

Preparation of Pd(η^5 -PhFCp)(η^3 -crotyl) (8c**).** Complex **8c** was synthesized as for **3b**, using the following compounds:

C₆₀Ph₅H (100 mg, 90.3 μ mol), ^tBuOK (1.0 M, 99.3 mL, 99.3 μ mol) in THF, [Pd(η^3 -crotyl)Cl]₂ (19.6 mg, 49.7 μ mol), and THF (10.0 mL). Yield: 60.0 mg (52%). ¹H NMR (400 MHz, CDCl₃): δ 0.51 (d, ³*J* = 6.4 Hz, 3H), 1.73 (d, ³*J* = 10.8 Hz, 1H), 2.67 (d, ³*J* = 6.4 Hz, 1H), 3.08 (dq, ³*J* = 10.8 Hz, ³*J* = 6.4 Hz, 1H), 4.66 (td, ³*J* = 10.8 Hz, ³*J* = 6.4 Hz, 1H), 7.20–7.25 (m, 15H), 7.88–7.90 (m, 10H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 18.31 (1C), 54.31 (1C), 59.13 (5C), 78.36 (1C), 101.32 (1C), 120.20 (5C), 127.14 (5C), 127.82 (10C), 128.30 (10C), 143.35 (10C), 145.30 (10C), 145.50 (5C), 146.68 (5C), 147.62 (10C), 148.59 (5C), 152.10 (10C). IR (powder, cm⁻¹): ν 3055 (m), 3022 (m), 2999 (w), 1949 (m), 1875 (m), 1795 (m), 1596 (m), 1583 (m), 1575 (m), 1491 (s), 1456 (s), 1444 (s), 1417 (m), 1376 (m), 1284 (m), 1264 (m), 1234 (m), 1202 (m), 1179 (m), 1155 (m), 1108 (m), 1070 (w), 1052 (w), 1030 (m), 1002 (w), 980 (w), 959 (m), 910 (m), 893 (m), 836 (m), 821 (w), 741 (m), 727 (s), 710 (m), 692 (s), 685 (s), 664 (s). UV-vis (1.0 \times 10⁻⁵ mol L⁻¹ in CH₂Cl₂; λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 258 (72 600), 278 (77 900, shoulder), 338 (34 500), 356 (31 900, shoulder), 394 (16 300, shoulder), 472 (4150, shoulder). HR-APCI-MS(−) (*m/z*): found, 1266.1564; calcd for **8c**, 1266.1567.

Preparation of Pt(η^5 -MeFCp)(η^3 -methallyl) (9**).** Complex **9** was synthesized as for **3b**, using the following compounds: C₆₀Me₅H (50.4 mg, 63.2 μ mol), ^tBuOK (1.0 M, 69.6 μ L, 69.6 μ mol) in THF, [Pt(η^3 -methallyl)Cl]₂ (19.9 mg, 34.8 μ mol), and THF (5.0 mL). Yield: **9**, 4.3 mg (6.5%); **5b**, 5.2 mg (9.7%). Data for **9** are as follows. ¹H NMR (400 MHz, CDCl₃): δ 2.38 (s, 15H), 2.66 (s with satellite, *J*_{Pt-H} = 27.2 Hz, 3H), 3.06 (s with satellite, *J*_{Pt-H} = 111.6 Hz, 2H), 4.40 (s with satellite, *J*_{Pt-H} = 63.6 Hz, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 23.52 (1C), 31.35 (satellite, *J*_{Pt-C} = 20.7 Hz, 5C), 33.22 (2C), 52.05 (5C), 92.60 (1C), 118.23 (5C), 144.34 (10C), 146.21 (10C), 147.40 (5C), 148.47 (10C), 149.28 (5C), 155.26 (10C). IR (powder, cm⁻¹): ν 2959 (m), 2916 (m), 2852 (m), 1729 (m), 1454 (m), 1439 (s), 1417 (m), 1378 (w), 1367 (m), 1264 (m), 1237 (m), 1213 (m), 1199 (m), 1156 (m), 1136 (m), 1111 (w), 1074 (w), 1036 (w), 1021 (m), 967 (w), 950 (w), 942 (w), 904 (m), 835 (m), 806 (m), 752 (s), 729 (s), 685 (s), 670 (m), 658 (s). UV-vis (7/3 toluene/2-propanol; nm): λ_{max} 285, 356 (shoulder), 393, 460 (shoulder). APCI-MS(+) (*m/z*): 1045 (M⁺). HR-APCI-MS(−) (*m/z*): found, 1045.1314; calcd for **9**, 1045.1375.

Data for **5b** are as follows. ¹H NMR (400 MHz, CDCl₃): δ 2.24 (s, 3H), 2.26 (s, 6H), 2.30 (s, 6H), 2.41 (s, 3H), 3.34 (2, 2H), 4.94 (s, 1H), 5.44 (s, 1H). ¹³C{¹H} NMR (100 MHz, 1/1 CDCl₃/CS₂): δ 25.03 (2C), 26.79 (2C), 26.99 (1C), 29.04 (1C), 44.72 (1C), 50.29 (2C), 52.50 (2C), 53.94 (1C), 62.29 (1C), 118.99 (1C), 139.23 (1C), 142.70 (2C), 143.18 (2C), 143.37 (1C), 143.75 (2C), 143.79 (2C), 144.10 (2C), 144.13 (2C), 144.20 (2C), 144.27 (2C), 144.47 (2C), 145.19 (2C), 145.19 (2C), 145.23 (2C), 145.96 (2C), 146.69 (2C), 147.41 (1C), 147.61 (2C), 147.70 (2C), 147.73 (2C), 147.84 (2C), 148.08 (2C), 148.18 (2C), 148.24 (2C), 148.44 (2C), 149.27 (2C), 153.31 (2C), 154.57 (2C), 155.35 (2C), 157.59 (2C). IR (powder, cm⁻¹): ν 2960 (m), 2918 (m), 2855 (m), 1727 (m), 1444 (s), 1417 (w), 1371 (w), 1286 (w), 1265 (w), 1238 (w), 1200 (w), 1172 (w), 1156 (w), 1130 (w), 1112 (w), 1104 (w), 1036 (w), 889 (m), 727 (s), 690 (m), 684 (s), 671 (m), 660 (m). UV-vis (7/3 toluene/2-propanol; nm): λ_{max} 286, 348, 360 (shoulder), 394, 470 (shoulder). HR-APCI-MS(−) (*m/z*): found, 850.1714; calcd for **5b**, 850.1722.

Preparation of Pt(η^5 -PhFCp)(η^3 -methallyl) (10**).** Complex **10** was synthesized as for **3b**, using the following compounds: C₆₀Ph₅H (50.0 mg, 45.2 μ mol), ^tBuOK (1.0 M, 49.7 μ L, 49.7 μ mol) in THF, [Pt(η^3 -methallyl)Cl]₂ (14.2 mg, 24.8 μ mol), and THF (5.0 mL). Yield: 8.6 mg (14%). ¹H NMR (400 MHz, CDCl₃): δ 1.97 (s with satellite, *J*_{Pt-H} = 32.1 Hz, 3H), 2.02 (s with satellite, *J*_{Pt-H} = 117.8 Hz, 2H), 3.29 (s with satellite, *J*_{Pt-H} = 64.6 Hz, 2H), 7.19 (m, 15H), 7.79 (d, ³*J* = 6.9 Hz, 10H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 29.83 (1C), 41.55 (2C), 58.88 (5C), 101.62 (1C), 120.30 (5C), 127.19 (5C), 127.66 (10C), 128.43 (10C), 142.96 (5C), 143.49 (10C), 145.01 (10C), 146.75 (5C), 147.65 (10C), 148.54 (5C), 151.67 (10C). IR

Table 4. Crystal Data and Structure Analysis Results for Complexes **7a,b** and **8a–c**

| | 7a ·CS ₂ | 7b ·1.5CS ₂ | 8a ·2.5CS ₂ | 8b ·0.25CS ₂ | 8c ·2CHCl ₃ |
|---|--|---|---|---|---|
| formula | C ₆₉ H ₂₀ Pd ₁ S ₂ | C _{70.50} H ₂₂ Pd ₁ S ₃ | C _{95.50} H ₃₀ Pd ₁ S ₅ | C _{94.25} H ₃₂ Pd ₁ S _{0.5} | C ₉₆ H ₃₄ Cl ₆ Pd ₁ |
| cryst syst | orthorhombic | monoclinic | triclinic | triclinic | triclinic |
| space group | <i>Pca</i> 2 ₁ (No. 29) | <i>P</i> 2 ₁ / <i>n</i> (No. 14) | <i>P</i> $\bar{1}$ (No. 2) | <i>P</i> $\bar{1}$ (No. 2) | <i>P</i> $\bar{1}$ (No. 2) |
| <i>R</i> , <i>R</i> _w (<i>I</i> > 2σ(<i>I</i>)) | 0.0683, 0.0693 | 0.0690, 0.0751 | 0.0609, 0.0661 | 0.0811, 0.2118 | 0.076, ^a – |
| <i>R</i> ₁ , <i>wR</i> ₂ (all data) | 0.1905, 0.1924 | 0.1735, 0.1827 | 0.1691, 0.1752 | 0.1114, 0.2541 | –, 0.115 |
| GOF on <i>F</i> ² | 1.071 | 1.111 | 1.025 | 1.063 | 2.543 |
| <i>a</i> , Å | 17.775(5) | 12.2190(5) | 13.5850(7) | 13.4150(11) | 13.742(2) |
| <i>b</i> , Å | 12.451(5) | 19.4580(8) | 13.5910(5) | 21.3700(12) | 13.943(2) |
| <i>c</i> , Å | 17.726(5) | 18.0680(6) | 19.2570(9) | 21.1590(16) | 18.661(3) |
| α, deg | 90 | 90 | 103.033(3) | 65.206(3) | 96.250(5) |
| β, deg | 90 | 101.240(3) | 95.960(2) | 80.338(3) | 94.407(5) |
| γ, deg | 90 | 90 | 117.024(2) | 78.855(4) | 116.421(6) |
| <i>V</i> , Å ³ | 3923(2) | 4213.4(3) | 2997(6) | 5377.1(7) | 3151.4(5) |
| <i>Z</i> | 4 | 4 | 2 | 4 | 2 |
| <i>T</i> , K | 153(2) | 120(2) | 120(2) | 153(2) | 298(2) |
| cryst size, mm | 0.88 × 0.52 × 0.12 | 0.80 × 0.42 × 0.05 | 0.32 × 0.20 × 0.12 | 0.45 × 0.18 × 0.12 | 0.40 × 0.20 × 0.10 |
| <i>D</i> _{calcd} , g cm ^{−3} | 1.726 | 1.689 | 1.600 | 1.589 | 1.588 |
| 2θ _{min} , 2θ _{max} , deg | 4.58, 51.22 | 4.18, 51.14 | 4.32, 51.56 | 4.26, 51.64 | 4.0, 55.0 |
| no. of rflns measd (unique) | 3322 | 7787 | 10 232 | 18 245 | 10 742 |
| no. of rflns measd (<i>I</i> > 2σ(<i>I</i>)) | 3225 | 7008 | 9162 | 12 391 | 9366 |
| no. of params | 650 | 674 | 925 | 1727 | 926 |
| Δ, e Å ^{−3} | 1.23, −1.75 | 1.29, −1.58 | 1.80, −1.00 | 1.78, −1.79 | 2.14, −1.49 |

^a A final *R* index is calculated with *I* > 3σ(*I*).

(powder, cm^{−1}): ν 2954 (m), 2922 (s), 2852 (m), 1733 (m), 1596 (m), 1492 (s), 1459 (s), 1445 (s), 1418 (w), 1378 (w), 1285 (w), 1263 (w), 1236 (w), 1202 (w), 1186 (w), 1156 (w), 1107 (w), 1071 (w), 1031 (m), 1021 (w), 1003 (w), 959 (m), 908 (m), 894 (w), 836 (w), 821 (w), 761 (m), 751 (m), 742 (m), 733 (s), 712 (m), 692 (s), 687 (m), 665 (m). UV–vis (7/3 toluene/2-propanol; nm): λ_{max} 285, 320 (shoulder), 357 (shoulder), 390, 460 (shoulder). HR-APCI-MS(−) (*m/z*): found, 1355.2092; calcd for **10**, 1355.2158.

X-ray Diffraction Studies. Crystals of **7a,b** and **8a–c** suitable for the X-ray diffraction study were mounted on a MacScience DIP2030 imaging plate diffractometer for data collection using Mo Kα (graphite monochromated, λ = 0.710 69 Å) radiation. Crystal data and data statistics are summarized in Table 4. The atomic parameters of most of the atoms for **7a,b** and **8a,b** were solved by the direct methods of SIR-97.³³ The positional parameters and thermal parameters of non-hydrogen atoms were refined anisotropically on *F*² by the full-matrix least-squares method, using SHELXL-97.³⁴ Hydrogen atoms were placed at calculated positions and refined “riding” on their corresponding carbon atoms. In the subsequent refinement, the function Σw(*F*_o² − *F*_c²)² was minimized, where |*F*_o| and |*F*_c| are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as *R*₁ = Σ(|*F*_o| − |*F*_c|)/Σ|*F*_o| and *wR*₂ = [Σw(*F*_o² − *F*_c²)²/Σ(w*F*_o⁴)]^{1/2}. The structure of **8c** was solved by direct methods and refined on *F*² by full-matrix least-squares calculations

using the maXus software package. The crotyl ligand of **8c** is disordered, assuming two orientations with site occupation parameters 0.70 and 0.30. Due to the disorder in the crotyl ligand, Pd–C1, Pd–C2, and Pd–C3 distances in **8c** have less certainty than those of **7a,b** and **8a,b**.

Electrochemical Measurements. Electrochemical measurements were performed using a BAS CV-50W voltammetric analyzer. A glassy-carbon electrode was used as the working electrode. The counter electrode was a platinum coil, and the reference electrode was a Ag/Ag⁺ electrode. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV/s. All half-wave potentials *E*_{1/2} = (*E*_{p,c} + *E*_{p,a})/2, where *E*_{p,c} and *E*_{p,a} are the cathodic and anodic peak potentials, respectively. The potential was corrected against Fc/Fc⁺.

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Supporting Information Available: Crystallographic details, including lists of positional parameters, thermal displacement parameters, bond lengths, and bond angles for **7a,b** and **8a–c**; data are also available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(33) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(34) Sheldrick, G. M. Program for the Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.