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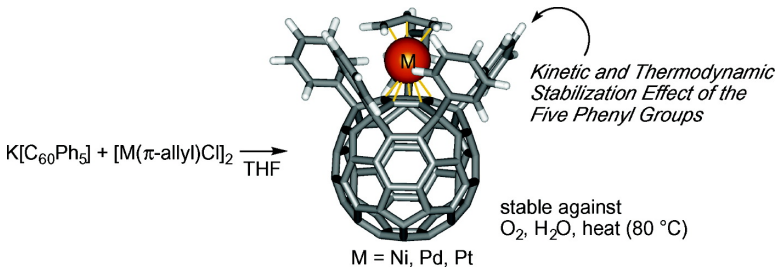

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Nickel, Palladium, and Platinum Complexes of η^5-Cyclopentadienide $C_{60}R_5$ Ligands. Kinetic and Thermodynamic Stabilization Effects of the $C_{60}Ph_5$ Ligand

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The nickel−, palladium−, and platinum−RFCp complexes Ni(η^5-RFCp)(η^3-allylic) (**3b**, RFCp = $C_{60}R_5$, R = Me, allylic = methallyl; **4a**, R = Ph, allylic = allyl; **4b**, R = Ph, allylic = methallyl), Pd(η^5-RFCp)(η^3-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(η^5-RFCp)(η^3-methallyl) (**9**, R = Me; **10**, R = Ph), were synthesized by transmetalation between K(RFCp) (R = Me, Ph) and [Ni(allylic)Br]$_2$, [Pd(allylic)Cl]$_2$, or [Pt(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(η^5-Cp)(η^3-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(η^5-$C_{60}R_5$)$(CO)_3$,[8] Fe(η^5-$C_{60}Me_5$)(η^5-C_5H_5),[9] Ru(η^5-$C_{60}Me_5$)L_n,[10,11] and Rh(η^5-$C_{60}Me_5$)$(CO)_2$[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 $C_{60}Ph_5$ ligand (PhFCp) and its thallium complex several years ago,[7a] we have so far been unable to synthesize

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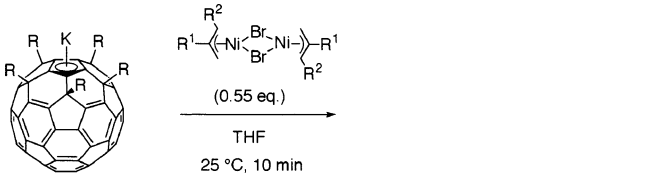
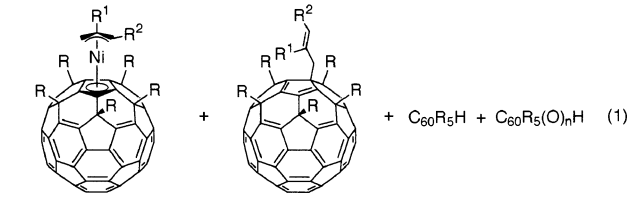
PhFCp transition-metal complexes, very likely because of steric congestion imposed by the five phenyl groups surrounding the cyclopentadienide moiety. This observation in turn suggested us that the PhFCp ligand may act to stabilize the otherwise unstable transition-metal complex by steric protection. 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-$C_{60}R_5$)(η^3-allylic) (allylic = allyl, methallyl, crotyl; R = Me, Ph) and Pt(η^5-$C_{60}R_5$)(η^3-methallyl) (R = Me, Ph), have also been synthesized and provide clues in understanding the origin of the stabilization effects of the C_{60}-Ph_5 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 C_5H_5 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 preparative 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 $C_{60}Me_5(CH_2CH{=}CH_2)$ (**5a**) in 22% yield. In the synthesis of **4a**, the allyl compound $C_{60}Ph_5(CH_2CH{=}CH_2)$ (**6a**) was also obtained as a side product in 6% yield. The remainder of the material balance was largely the starting material $C_{60}Ph_5H$ (85%) and its oxidation products[17] (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]





3b: 8% (R = Me, R^1 = Me, R^2 = H)	0% (R = Me, R^1 = Me, R^2 = H)	31% (R = Me)	60% (R = Me)
4a: 4% (R = Ph, R^1 = R^2 = H)	**6a**: 6% (R = Ph, R^1 = R^2 = H))	85% (R = Ph)	5% (R = Ph)
4b: 22% (R = Ph, R^1 = Me, R^2 = H)	0% (R = Ph, R^1 = Me, R^2 = H)	ND[a] (R = Ph)	ND[a] (R = Ph)

ND[a] = no data

Structure assignment was achieved by the standard physical methods. High-resolution APCI-TOF-MS(+) data were consistent with the assigned structures. The ^{1}H and ^{13}C NMR measurements of nickel complexes **3b** and **4a**,**b** indicated that the FCp moieties have C_{5v} symmetry. For instance, the ^{13}C NMR spectrum displayed only eight signals due to the C_{5v}-symmetric fullerene skeleton: the cyclopentadienyl moiety (δ 111.88), the sp^3 fullerene carbon atom (δ 51.01), the sp^2 carbon atom next to the sp^3 carbon (δ 154.19), and five other types of fullerene sp^2 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 (CH_3), 44.20 (CH_2), and 100.51 (center carbon)). Therefore, the rotation of the FCp moiety around the Ni−FCp axis and the five addends on the fullerene sp^3 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 atom followed by reductive elimination of allylcyclopentadiene.

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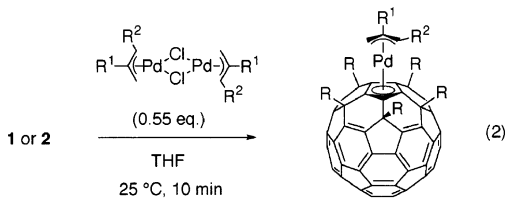
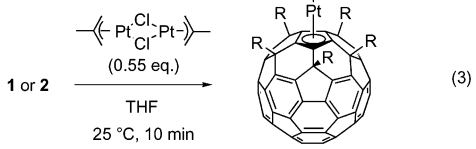
The syntheses followed those of the nickel complexes. The palladium and platinum allyl and methallyl complexes Pd(η^5-RFCp)(η^3-allylic) (**7a**, allylic = allyl, R = Me; **7b**, allylic = methallyl, R = Me; **7c**, allylic = crotyl, R = Me; **8a**, allylic = allyl, R = Ph; **8b**, allylic = methallyl, 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]$_2$[20] (eqs 2 and 3). After



7: R = Me
7a: $R^1 = R^2 = H$ 21%
7b: R^1 = Me, R^2 = H 55%
7c: R^1 = H, R^2 = Me 21%
8: R = Ph
8a: $R^1 = R^2 = H$ 48%
8b: R^1 = Me, R^2 = H 71%
8c: R^1 = H, R^2 = Me 52%



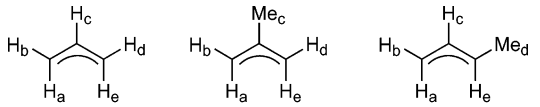
9: R = Me 6.5%
10: R = Ph 14%

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, $C_{60}Me_5(CH_2CH{=}CH_2)$ (**5a**), $C_{60}Ph_5(CH_2CH{=}CH_2)$ (**6a**), and $C_{60}Me_5(CH_2C(Me){=}CH_2)$ (**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 $C_{60}Me_5(CH_2C(Me){=}CH_2)$ (**5b**) upon heating.

Identification of these palladium and platinum complexes was achieved by high-resolution APCI-TOF-MS(+) and ^{1}H and ^{13}C NMR measurements. The ^{1}H 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 ^{1}H NMR Chemical Shifts (ppm) between π-Allylic Ligands of Palladium Complexes 7a−c and 8a−c



7a, **8a** (η^3-allyl) **7b**, **8b** (η^3-methallyl) **7c**, **8c** (η^3-crotyl)

	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		4.06		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_5Me_5)	1.91	2.96	4.75				
Pd(η^3-allyl)(η^5-C_5Ph_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−C_5Ph_5 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 C_5Me_5 to the C_5Ph_5 compound in a simple Cp series; namely, the proton signals of the π-allyl moiety of the C_5Ph_5 palladium complex Pd(η^5-C_5Ph_5)(η^3-allyl)[19d] appears at lower magnetic field (δ 1.91, 2.96, and 4.75) than those of the C_5Me_5 palladium complex Pd(η^5-C_5Me_5)(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 CS_2/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

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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 sp^3 carbon atoms, within the fullerene skeleton.

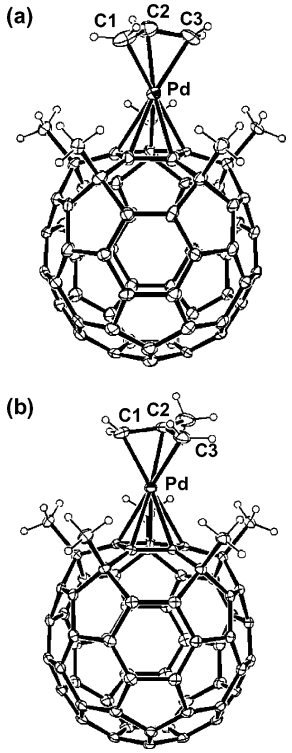

Figure 1. Molecular structures of the Pd−MeFCp complexes with 30% probability level ellipsoids: (a) **7a**·CS_2; (b) **7b**·1.5CS_2. The solvent molecules in the unit cell are omitted for clarity.

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)(CH_3)$(CO)_2$,[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)(CH_3)$(CO)_2$,[10] Rh(η^5-MeFCp)-$(CO)_2$,[12] and $C_{60}Ph_5H$.[24] We therefore consider that the reduction puts the electron into the fullerene moiety.

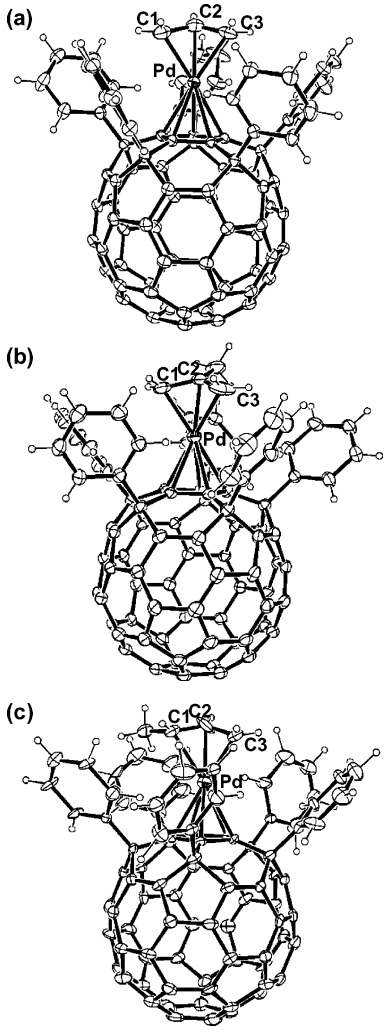

Figure 2. Molecular structures of the Pd−PhFCp complexes with 30% probability level ellipsoids: (a) **8a**·2.5CS_2; (b) **8b**·0.25CS_2; (c) **8c**·2$CHCl_3$. The solvent molecules in the unit cell are omitted for clarity.

The electron-withdrawing effect of the five phenyl groups makes the reduction of the PhFCp complex **8a** ($E_{1/2}^{red1} = -1.40$ V) easier than that of the MeFCp complex **7a** ($E_{1/2}^{red1} = -1.47$ 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**$^{\bullet-}$. 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-

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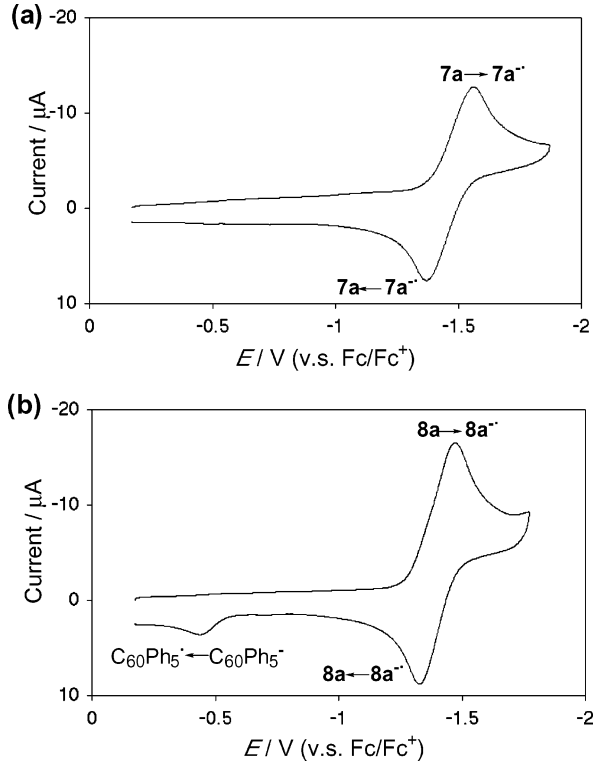

Figure 3. Cyclic voltammograms of the palladium−RFCp π-allyl complexes: (a) reversible one-electron reduction of **7a**; (b) irreversible one-electron reduction of **8a**. Both measurements were carried out in a 1.0 mM THF solution containing 100 mM [^{n}Bu$_4$N][ClO$_4$] as a supporting electrolyte.

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

	$E_{1/2}^{red}$(1) (V)	$E_{1/2}^{red}$(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
$C_{60}Me_5H$[e]	−1.48	−2.07
$C_{60}Ph_5H$[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 group[25] would be useful. "Thermodynamic" stabilization may also play a role: 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. $C_{60}Me_5H$ and $C_{60}Ph_5H$ were prepared according to the literature.[7] A THF solution of ^{t}BuOK 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]$_2$[20] 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 ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL EX-400 spectrometer. Proton chemical shifts are reported relative to Me$_4$Si (CDCl$_3$) at δ 0.00 ppm or residual solvent signals (CDCl$_3$ at δ 7.26 ppm; THF-d_8 at δ 1.73 and 3.58 ppm). Carbon chemical shifts are reported relative to CDCl$_3$ 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 $C_{60}Me_5H$ (50.0 mg, 62.7 μmol) in THF (5.0 mL) was added a solution of ^{t}BuOK (1.0 M, 69.0 μL, 69.0 μmol) in THF. To the resulting dark reddish orange solution was added [Ni(η^3-methallyl)Br]$_2$ (13.4 mg, 34.5 μmol). The reaction mixture was stirred at 25 °C for 10 min before being quenched by addition of saturated aqueous NH$_4$Cl (1.0 mL). The mixture was diluted with toluene and washed with water. The organic layer was dried over MgSO$_4$ 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. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.29 (s, 3H), 2.30 (s, 15H), 2.54 (s, 2H), 3.61 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): 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

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(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: C_{60}-Ph_5H (50.0 mg, 45.2 μmol), ^{t}BuOK (1.0 M, 49.7 μL, 49.7 μmol) in THF, [Ni(η^3-methallyl)Br]$_2$ (8.93 mg, 24.8 μmol), and THF (1.0 mL). Yield: 2.2 mg (4.0%). ^{1}H 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). $^{13}C\{^1H\}$ 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. ^{1}H 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). ^{1}H NMR (400 MHz, 1/3 $CDCl_3/CS_2$): 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). $^{13}C\{^1H\}$ NMR (100 MHz, 1/3 $CDCl_3/CS_2$): 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, M^{-1} cm^{-1})): 260 (81 800, shoulder), 272 (75 100, shoulder), 354 (22 300, shoulder), 395 (11 800, shoulder), 474 (4310, shoulder). APCI-MS(±) (*m*/*z*): = 1147 ($[M + H]^+$), 1146 (M^-). Anal. Calcd for **6a**·$0.5CS_2$: 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: $C_{60}Ph_5H$ (10.0 mg, 9.03 μmol), ^{t}BuOK (1.0 M, 10.0 μL, 10.0 μmol) in THF, [Ni(η^3-methallyl)Br]$_2$ (1.92 mg, 4.97 μmol), and THF (1.0 mL). Yield: 2.4 mg (22%). ^{1}H 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). $^{13}C\{^1H\}$ 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 (shoulder). 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: C_{60}-Me_5H (100 mg, 125 μmol), ^{t}BuOK (1.0 M, 138 μL, 138 μmol) in THF, [Pd(η^3-allyl)Cl]$_2$ (25.2 mg, 68.9 μmol), and THF (10.0 mL). Yield: 25 mg (21%). ^{1}H 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). $^{13}C\{^1H\}$ 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, M^{-1} 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**·$0.5CS_2$: 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. ^{1}H 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). ^{1}H NMR (400 MHz, 1/3 $CDCl_3/CS_2$): 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). $^{13}C\{^1H\}$ NMR (100 MHz, 1/3 $CDCl_3/CS_2$): 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, M^{-1} cm^{-1})): 255 (66 800, shoulder), 348 (21 900), 356 (20 600, shoulder), 396 (12 500), 476 (3450, shoulder). APCI-MS(+) (*m*/*z*): 837 ($[M + H]^+$). Anal. Calcd for **5a**·$0.5CS_2$: 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: $C_{60}Me_5H$ (100 mg, 125 μmol), ^{t}BuOK (1.0 M, 138 μL, 138 μmol) in THF, [Pd(η^3-methallyl)Cl]$_2$ (27.2 mg, 68.9 μmol), and THF (10.0 mL). Yield: 66.0 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 15H), 2.36 (s, 3H), 2.94 (s, 2H), 4.25 (s, 2H). ^{1}H NMR (400 MHz, THF-d_8): δ 2.38 (s, 15H), 2.46 (s, 3H), 3,05 (s, 2H), 4.39 (s, 2H). $^{13}C\{^1H\}$ 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). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): 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, M^{-1} 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: $C_{60}Me_5H$ (100 mg, 125 μmol), ^{t}BuOK (1.0 M, 138 μL, 138 μmol) in THF, [Pd(η^3-crotyl)Cl]$_2$ (27.2 mg, 68.9 μmol), and THF (10.0 mL). Yield: 25.6 mg (21%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.02 (d, ^3J = 6.0 Hz, 3H), 2.34 (s, 15H), 2.81 (d, ^3J = 10.8 Hz, 1H), 4.06 (dq, ^3J = 10.8 Hz, 1H), 4.10 (d, ^3J = 6.4 Hz, 1H), 5.41 (ddd, ^3J = 10.8 Hz, ^3J = 10.8 Hz, ^3J = 6.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 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 (1.0×10^{-5} mol L^{-1} in CH_2Cl_2; 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: $C_{60}Me_5H$ (100 mg, 90.3 μmol), ^{t}BuOK (1.0 M, 99.3 μL, 99.3 μmol) in THF, [Pd(η^3-crotyl)Cl]$_2$ (18.2 mg, 49.7 μmol), and THF (10.0 mL). Yield: **8a**, 54.3 mg (48%); **6a**, 9.5 mg (9.2%). Data for **8a** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.09 (d, ^3J = 11.2 Hz, 2H), 3.08 (d, ^3J = 6.4 Hz, 2H), 4.70 (tt, ^3J = 11.2 Hz, ^3J = 6.4 Hz, 1H), 7.16−7.20 (m, 15H), 7.77−7.79 (m, 10H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 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 (1.0×10^{-5} mol L^{-1} in CH_2Cl_2; 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**·0.5C_7H_8: 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: $C_{60}Ph_5H$ (100 mg, 90.3 μmol), ^{t}BuOK (1.0 M, 99.3 μL, 99.3 μmol) in THF, [Pd(η^3-methallyl)Cl]$_2$ (19.6 mg, 49.7 μmol), and THF (10.0 mL). Yield: 81.6 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 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 (1.0×10^{-5} mol L^{-1} in CH_2Cl_2; 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**·0.25CS_2: 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: $C_{60}Ph_5H$ (100 mg, 90.3 mmol), ^{t}BuOK (1.0 M, 99.3 mL, 99.3 mmol) in THF, [Pd(η^3-crotyl)Cl]$_2$ (19.6 mg, 49.7 mmol), and THF (10.0 mL). Yield: 60.0 mg (52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.51 (d, ^3J = 6.4 Hz, 3H), 1.73 (d, ^3J = 10.8 Hz, 1H), 2.67 (d, ^3J = 6.4 Hz, 1H), 3.08 (dq, ^3J = 10.8 Hz, ^3J = 6.4 Hz, 1H), 4.66 (td, ^3J = 10.8 Hz, ^3J = 6.4 Hz, 1H), 7.20−7.25 (m, 15H), 7.88−7.90 (m, 10H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 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 (1.0×10^{-5} mol L^{-1} in CH_2Cl_2; 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: $C_{60}Me_5H$ (50.4 mg, 63.2 μmol), ^{t}BuOK (1.0 M, 69.6 μL, 69.6 μmol) in THF, [Pt(η^3-methallyl)Cl]$_2$ (19.9 mg, 34.8 μmol), and THF (5.0 mL). Yield: **9**, 4.3 mg (6.5%); **5b**, 5.2 mg (9.7%). Data for **9** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 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. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C{^{1}H} NMR (100 MHz, 1/1 $CDCl_3$/CS_2): 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: $C_{60}Ph_5H$ (50.0 mg, 45.2 μmol), ^{t}BuOK (1.0 M, 49.7 μL, 49.7 μmol) in THF, [Pt(η^3-methallyl)Cl]$_2$ (14.2 mg, 24.8 μmol), and THF (5.0 mL). Yield: 8.6 mg (14%). ^{1}H NMR (400 MHz, $CDCl_3$): 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, ^3J = 6.9 Hz, 10H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 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**·2$CHCl_3$
formula	$C_{69}H_{20}Pd_1S_2$	$C_{70.50}H_{22}Pd_1S_3$	$C_{95.50}H_{30}Pd_1S_5$	$C_{94.25}H_{32}Pd_1S_{0.5}$	$C_{96}H_{34}Cl_6Pd_1$
cryst syst	orthorhombic	monoclinic	triclinic	triclinic	triclinic
space group	$Pca2_1$ (No. 29)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
R, R_w ($I > 2\sigma(I)$)	0.0683, 0.0693	0.0690, 0.0751	0.0609, 0.0661	0.0811, 0.2118	0.076,[a] −
R1, wR2 (all data)	0.1905, 0.1924	0.1735, 0.1827	0.1691, 0.1752	0.1114, 0.2541	−, 0.115
GOF on F^2	1.071	1.111	1.025	1.063	2.543
a, Å	17.775(5)	12.2190(5)	13.5850(7)	13.4150(11)	13.742(2)
b, Å	12.451(5)	19.4580(8)	13.5910(5)	21.3700(12)	13.943(2)
c, 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)
V, Å^3	3923(2)	4213.4(3)	2997(6)	5377.1(7)	3151.4(5)
Z	4	4	2	4	2
T, 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
D_{calcd}, g cm^{-3}	1.726	1.689	1.600	1.589	1.588
$2\theta_{min}$, $2\theta_{max}$, 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 ($I > 2\sigma(I)$)	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 $I > 3\sigma(I)$.

(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, $\lambda = 0.710\ 69$ 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 $\sum w(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as R1 = $\sum(||F_o| - |F_c||)/\sum|F_o|$ and wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$. 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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