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Preparations, NMR Spectra, and Electrochemical Properties of a (Ferrocenylcarbonyl)palladium(II) Complex and Its Derivatives with Some Chelate Groups Attached via Two Ligating Nitrogen Atoms

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Oxidative addition of (chloroformyl)ferrocene to $[\mathrm{Pd(PPh_3)_4}]$ yielded a stable acylpalladium(II) compound of $[\mathrm{Pd(COFc)Cl(PPh_3)_2}]$ (**1**), (Fc=ferrocenyl). Complex **1** was treated with alkali metal salts of poly(1-pyrazolyl)-borates ($\mathrm{H}_n\mathrm{BPz}_{4-n}$), (Pz=1-pyrazolyl) to give complexes $[\mathrm{Pd(COFc)(H}_n\mathrm{BPz}_{4-n})(\mathrm{PPh_3})]$, (**2**, n=0; **3**, n=1; and **4**, n=2), which retained the palladium-attached ferrocenylcarbonyl structure. Reaction of **1** with 1,10-phenanthroline (phen) afforded [Pd(COFc)Cl(phen)], whereas reaction with 2,2′-bipyridine gave $[\{\mathrm{Pd(COFc)Cl(PPh_3)}\}_2]$ as an isolable material. Transformation of the ferrocenylcarbonyl moiety took place to the ferrocenyl group on palladium, in chlorine-abstraction from **1** with $\mathrm{AgClO_4 \cdot H_2O}$ in $\mathrm{CH_3CN}$. In the temperature-dependent ^{1}H-NMR spectra, fluxional behavior was observed for the poly(1-pyrazolyl)borate groups in **2** and **3**. Electrochemical experiments were carried out for **1**—**4** in $\mathrm{CH_3CN}$ using platinum working electrodes, and reversible one-electron redox-couples were detected, which were attributed to the process $\mathrm{Fe(II)} \rightleftarrows \mathrm{Fe(III)}$ in the ferrocenyl moiety. Furthermore, electron-withdrawing effects of the [poly(1-pyrazolyl)borato]palladiocarbonyl moieties from the Fe centers were compared among these complexes, in relation to their redox potentials.

Transition-metal acyl complexes have been regarded as models of intermediates for catalytic hydroformylation and carboxylation of olefins.[1—6] It would be still worthwhile to synthesize new stable acyl complexes and to study their chemical reactivity and stability of the acyl-metal σ-bonds, in relation to the properties of coexisting other ligands and to the character of alkyl or aryl groups in the acyl moiety. In the course of our study on the properties and applications of bimetallic complexes with ferrocene moieties,[7] we performed oxidative addition of (chloroformyl)ferrocene to tetrakis(triphenylphosphine)palladium(0) $[\mathrm{Pd(PPh_3)_4}]$ to yield a stable complex of chloro(ferrocenylcarbonyl)bis(triphenylphosphine)palladium(II) $[\mathrm{Pd(COFc)Cl(PPh_3)_2}]$ (Fc=ferrocenyl) (**1**), which involved the well-delocalized π-system of the ferrocenylcarbonyl group. The present paper deals with the syntheses, NMR spectra, and electrochemical properties of the complex **1** and its derivatives with some chelates attached via two ligating nitrogen atoms, including poly(1-pyrazolyl)-borate groups $[\mathrm{H}_n\mathrm{BPz}_{4-n}]^-$ (Pz=1-pyrazolyl).[8—10] Poly(1-pyrazolyl)borate groups are a versatile and interesting class of uninegative ligands, which have been shown to confer considerable stability on organometallic complexes and have a potentiality for novel fluxionality on the basis of NMR spectroscopy. Electrochemical properties of these groups seemed to be one of key clues to their interesting character. To our knowledge, there were no reports on the electrochemistry of transition-metal poly(1-pyrazolyl)-borate complexes except Trofimenko's brief mention on the polarographic data of $[\mathrm{M(H}_n\mathrm{BPz}_{4-n})_2]$ (M=Fe, Co, and Cu).[9]

Results and Discussion

Syntheses and Properties of (Ferrocenylcarbonyl)palladium(II) Complexes. When the zerovalent palladium compound $[\mathrm{Pd(PPh_3)_4}]$ was added to a benzene solution of (chloroformyl)ferrocene, the color turned into orange and the resulting yellowish orange precipitates were found to be the (ferrocenylcarbonyl)palladium(II) complex **1**. In the IR spectrum, there were a strong ν(C=O) band at 1655 $\mathrm{cm^{-1}}$ and a medium ν(Pd–Cl) band at 303 $\mathrm{cm^{-1}}$. The ^{13}C-NMR spectrum of **1** in $\mathrm{CD_2Cl_2}$ showed a weak signal for the carbonyl carbon at δ=207.9. A large signal at δ=69.8 was attributed to the unsubstituted cyclopentadienyl group, and three resonances at δ=70.5, 71.1, and 73.1 were to the monosubstituted one. The phenyl carbons in the coordinated triphenylphosphine ligands resonated at δ=129.7 (1-C), 135.0 (2-C), 128.4 (3-C), and 132.3 (4-C).

Treatment of **1** with sodium or potassium salts of poly(1-pyrazolyl)borates $[\mathrm{H}_n\mathrm{BPz}_{4-n}]^-$ yielded (ferrocenylcarbonyl)[poly(1-pyrazolyl)borato]palladium(II) $[\mathrm{Pd(COFc)(H}_n\mathrm{BPz}_{4-n})(\mathrm{PPh_3})]$ (**2**, n=0; **3**, n=1; and **4**, n=2). Complexes **2** and **3** were considerably air-stable both in the solid states and in common organic solvents. On the other hand, complex **4** was slowly decomposed in halogenated solvents, and solubility in other organic solvents, such as benzene and THF was a little lower than those of **1**—**3**. Similar decomposition and low solubility of palladium complexes with the $\mathrm{H_2BPz_2}$ group were reported previously.[9,10] Characteristic ν(C=O) bands were observed for **2**—**4** near 1650 $\mathrm{cm^{-1}}$ similarly to that of **1**, supporting retention of the palladium-attached ferrocenylcarbonyl structure in these complexes. The

Table 1. Yields, Analytical Data, and Properties of Complexes

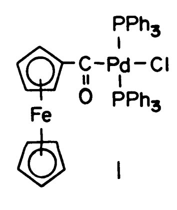
Complex		Yield[a] %	Found (Calcd)(%) C	H	N	Mp[b] θ_m/°C	ν(C=O)[c] cm^{-1}
[Pd(COFc)Cl(PPh$_3$)$_2$][d]	**1**	80[e]	64.26 (64.19)	4.55 (4.47)	0.00 (0.00)	165—170	1655
[Pd(COFc)(BPz$_4$)(PPh$_3$)]	**2**	46	57.02 (57.21)	4.23 (4.22)	12.95 (13.02)	192—196	1650
[Pd(COFc)(HBPz$_3$)(PPh$_3$)]	**3**	41	57.15 (57.43)	4.46 (4.31)	10.29 (10.57)	174—180	1643
[Pd(COFc)(H$_2$BPz$_2$)(PPh$_3$)]	**4**	30	57.40 (57.69)	4.46 (4.43)	7.59 (7.69)	164—168	1648
[Pd(COFc)Cl(phen)][f]	**5**	53	52.02 (51.63)	3.29 (3.20)	4.89 (5.24)	188—191	1660
[{Pd(COFc)Cl(PPh$_3$)}$_2$][g]	**6**	42	56.84 (56.44)	4.20 (3.92)	0.00 (0.00)	185—188	1660

a) Based on **1**, unles noted elsewhere. b) Uncorrected value; with decomposition in a capillary tube. c) Measured in KBr disc. d) ν(Pd–Cl), 314(sh) and 303 cm^{-1}. e) Based on [Pd(PPh$_3$)$_4$]. f) ν(Pd–Cl), 322 (sh) and 311 cm^{-1}. g) Far IR data, 353(s), 326(m), 313(m), 302(m), and 264(m) cm^{-1}.

Table 2. ^{1}H-NMR Data of the (Ferrocenylcarbonyl)palladium(II) Complexes[a]

Complex	(η^5-C$_5$H$_4$)-CO-Pd (2-H, 5-H)	(3-H, 4-H)	η^5-C$_5$H$_5$	1-Pyrazolyl group 3-H	4-H	5-H
1	4.40(bs)	4.06(t, 2.0)	3.64(s)	—	—	—
2[b]	3.95(bs)	3.95(bs)	3.95(bs)	7.24(d, 2.0)	6.32(bs)	d)
3	4.0 (bs)	3.7 (bs)	3.73(s)	7.36(bs)	6.17(t, 2.0)	7.69(d, 2.0)
4[c]	4.10(bs)	3.98(bs)	3.77(s)	5.81(bs) 6.13(dd, 2.0, 0.5)	5.58(t, 2.0) 6.00(dt, 2.0, 0.8)	8.07(d, 2.0) d)

a) Measured in CDCl$_3$ at 23 °C with the CW-type JNM-MH-100 spectrometer, unless stated otherwise; δ values from TMS; signal shape and coupling constants in Hz are given in the parentheses; abbreviations used, s=singlet, bs=broad singlet, dd=doublet of doublets d=doublet, t=triplet, dt=doublet of triplets. b) At 51 °C. c) In toluene-d^8; measured with the FT-type FX-90-Q spectrometer. d) Obscured by signals for PPh$_3$.



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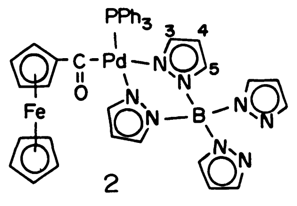

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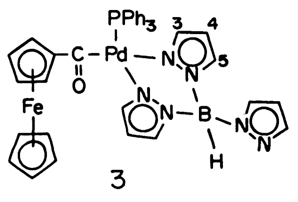

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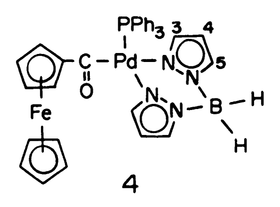

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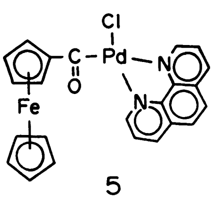

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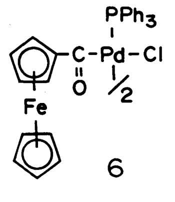

6

HBPz$_3$ group in **3** showed a ν(BH) band at 2450 cm^{-1}, and the H$_2$BPz$_2$ group in **4** gave a characteristic ν(BH$_2$) pattern consisting of a slightly resolved doublet at 2395 cm^{-1} and a weak band at 2280 cm^{-1}. Visible absorption spectra of **1**—**4** in CH$_3$CN showed a band around 460 nm, which was associated with the mixing of a charge-transfer type transition from the Fe atom to the antibonding orbitals on the cyclopentadienyl rings and a d-d type transition.[7]

In addition, complex **1** was treated with 1,10-phenanthroline (phen), and the complex [Pd(COFc)-Cl(phen)] (**5**) was formed through displacement of two triphenylphosphine molecules. Complex **5** was very insoluble in benzene and dichloromethane, and a ^{1}H-NMR spectrum was not obtained. In case of the reaction with 2,2′-bipyridine (bpy), the expected compound [Pd(COFc)Cl(bpy)] was not isolated, and the reaction-mixture gave a very insoluble material (**6**). Although NMR measurement was not possible, the IR spectrum confirmed retention of the ferrocenylcarbonyl group and triphenylphosphine on palladium. The elemental analysis of **6** suggested its structure to be $[\{Pd(COFc)Cl(PPh_3)\}_2]$,[11] and one mole of triphenylphosphine remained coordinated to the palladium atom in the marked contrast to the case of phen.

Chlorine-abstraction from **1** in CH_3CN was performed with hydrated silver perchlorate in expectation of a cationic complex $[Pd(COFc)(NCCH_3)(PPh_3)_2]ClO_4$, and a pale yellow material (mp, 186 °C (decomp)) of (**7**)[14] was obtained from the reaction-mixture. The IR spectrum of **7** did not show any ν(C=O) bands. There was a strong band at 1095 cm^{-1} without any significant splitting, assignable to the T_2(ClO) stretching mode of an ionic perchlorate uncomplexed. Measurement of the ^{1}H-NMR spectrum indicated retention of the ferrocenyl group and triphenylphosphine in a ratio close to 1:2. The above evidence led us to believe that the ferrocenyl group migrated to the vacant coordination-site produced, followed by dissociation of carbon monoxide from palladium.[1,2] The resulting vacant site seemed to be occupied by a water molecule.

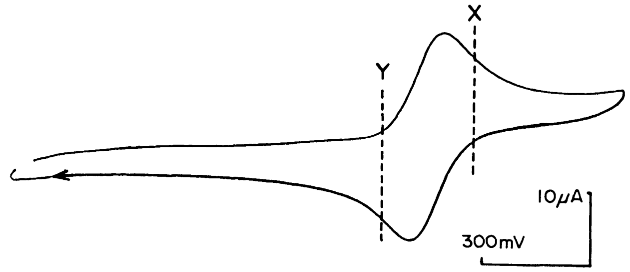

Fig. 1. Cyclic voltammogram of 10^{-3} mol dm^{-3} [Pd(COFc)(BPz$_4$)(PPh$_3$)] in CH_3CN at a scan rate of 100 mV/s.

Fluxional Behavior of (Ferrocenylcarbonyl)[poly(1-pyrazolyl)borato]palladium(II) Complexes. In ^{1}H-NMR spectra of **2** measured in $CDCl_3$ at 51 °C, four pyrazolyl groups in the BPz$_4$ ligand exhibited a slightly broad singlet (4H) at δ=6.32 for 4-H's and a doublet (4H) at δ=7.24 for 3-H's, as shown in Table 2. However, a signal for 5-H's was obscured by those for triphenylphosphine and was not determined explicitly. Upon cooling to −30 °C, the broad singlet for 4-H's separated into three triplets (1H, 2.0 Hz) at δ=5.71, 6.18, and 6.36, and one slightly broad singlet (1H) at δ=6.31. The 3-H protons resonated as three slightly broad singlets at δ=6.59 (2H), 6.77 (1H), and 7.06 (1H). Concerning 5-H's, two slightly broad singlets were observed at δ=7.71 (1H) and 7.93 (2H), whereas a signal of the remaining proton was not distinguished owing to overlapping with the aromatic protons in triphenylphosphine. At this temperature, coordination of the BPz$_4$ ligand to palladium was stereochemically rigid to give the four spectroscopically nonequivalent pyrazolyl groups. On the other hand at 51 °C, fluxional motion of the BPz$_4$ ligand averaged environments of all pyrazolyl groups leading to their spectroscopic equivalence.

As described previously,[15–17] the geometrical arrangement in the stereochemically rigid coordination has a square-planar structure about the central palladium atom and a boat conformation of the Pd–(pyrazolyl)$_2$–B six-membered ring. The fluxional motion for the spectroscopic equivalence of four pyrazolyl groups at high temperatures has been regarded as the "tumbling process", which involves coordination of the uncoordinated pyrazolyl group near the palladium atom, accompanied instantaneously by dissociation of the previously coordinated group and by inversion of the Pd-(pyrazolyl)$_2$-B ring.

As for the monosubstituted cyclopentadienyl group in **2**, a broad singlet at δ=3.95 was observed at 51 °C, which overlapped a signal of the unsubstituted cyclopentadienyl group.

^{1}H-NMR spectra of the [hydrotris(1-pyrazolyl)-

Table 3. Electrochemistry of Complexes **1**—**4** and Electronic Spectra of Their Oxidized Species

Complex	Electrochemical data[a]				Oxidized species	
	$E°$ / mV	ΔE_p / mV	i_{pc}/i_{pa}	n[b] (Found)	λ_{max} / nm	ε / mol^{-1} dm^3 cm^{-1}
1	159	62	0.94	1.12	623	310
2	119	62	0.99	0.98	631	309
3	105	62	0.91	1.08	625	235
4	104	147	0.95	~1.0[c]	625	214

a) In CH_3CN; $(n\text{-}Bu_4N)PF_6$=0.1 mol dm^{-3}; complex=10^{-3} mol dm^{-3}; scan rate=100 mV/s; redox for the Fe(II)$\rightleftarrows$Fe(III) couple; see the text and ref. 18. b) Number of electrons passed per complex, for anodic exhaustive electrolysis. c) Corresponding to the first step, see the text.

borato]palladium(II) **3** in $CDCl_3$ at 23 °C showed a triplet (3H) δ=6.17 for 4-H's, a slightly broad singlet (3H) at δ=7.36 for 3-H's, and a doublet (3H) at δ=7.69 for 5-H's, indicating spectroscopic equivalence of all pyrazolyl groups and fluxional behavior of the $HBPz_3$ ligand. On cooling to −45 °C, the signals for pyrazolyl groups became broader gradually, but a slow-exchange limiting spectrum was not obtained. Similar difficult fixation of the fluxional motion of the $HBPz_3$ ligand on cooling was described previously in some [hydrotris(1-pyrazolyl)borato]palladium(II) complexes.[16,17]

^1H-NMR spectra of the [dihydrobis(1-pyrazolyl)-borato]palladium(II) **4** were measured in toluene-d^8 in the temperature range of 50 to −36 °C, and there was no spectral change observed. At 80 °C, the complex was decomposed slowly. Two 4-H protons at room temperature resonated as triplets at δ=5.58 and 6.00, and two 3-H protons did as a slightly broad singlet at δ=5.81 and a doublet at δ=6.13. Additional smaller coupling to ^{31}P nucleus was noticed for the signals at δ=6.00 and 6.13 in the FT-type NMR measurement, and suggested that protons for these two signals belonged to the pyrazolyl group at a trans position to the triphenylphosphine ligand. Concerning 5-H's, one proton appeared as a doublet at δ=8.07, but the other one was obscured by overlapping with the signals of triphenylphosphine. As a whole, complex **4** did not show the fluxional motion involving bond-breaking process between palladium and pyrazolyl groups.

Electrochemistry of (Ferrocenylcarbonyl)palladium(II) Complexes. Acetonitrile solutions of complexes **1**—**4** were served for their electrochemical studies, containing 0.1 mol dm^{-3} $(n\text{-}Bu_4N)PF_6$ as supporting electrolyte. Working electrodes were a platinum disc and gauze for cyclic voltammetry and bulk electrolysis, respectively. Cyclic voltammogram in Fig. 1 shows a typical well-reversible redox-couple for **2**. The peak current ratio of i_{pc}/i_{pa} remained close to unity in the sweep rate of 200 to 10 mV/s, and the current function (proportional to $i_p/\sqrt{v}$) was also constant with the rate.[18] There was no current flow observed in the bulk electrolysis at the controlled potential Y in Fig. 1. On the other hand, the electrolysis at X resulted in an anodic current, which upon integration yielded charge consistent with one electron per molecule of the complex, and changed color of the solution from yellowish orange to dark brown. One-electron transfer was also confirmed by potential separation ΔE_p between oxidation and reduction peaks of the couple, which was very close to theoretical 59 mV. These findings indicated that the redox under consideration was electrochemically reversible and diffusion-controlled one-electron transfer, and that the oxidation product of **2** was stable during the time of the sweep.[19,20] Complexes **1** and **3** underwent analogous reversible one-electron oxidation, and the results are summarized in Table 3.

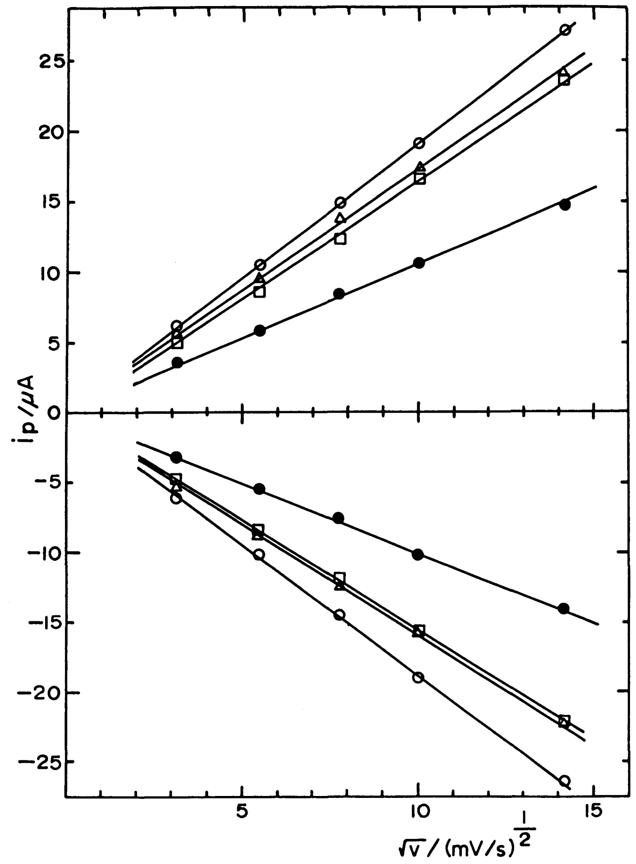

Fig. 2. Dependence of anodic and cathodic peak currents i_p of the Fe(III)/Fe(II) redoxes on the scan rate v. Concentration of complexes; 10^{-3} mol dm^{-3} ●: Complex **1**, ○: Complex **2**, △: Complex **3**, □: Complex **4**.

The corresponding redox-couple for **4** with the H_2BPz_2 group demonstrated that the peak current ratio i_{pc}/i_{pa} was nearly close to unity and the current function was also independent of the sweep rate similarly, whereas the peak separation ΔE_p was fairly larger than the theoretical 59 mV on the contrary. Thus, the redox couple of **4** was diffusion-controlled like the other complexes, but varying in the electrochemical reversibility, and was regarded as quasi-reversible.[19,20] Furthermore, the bulk electrolysis of **4** (10^{-3} mol dm^{-3}) was performed at a slightly more anodic potential than that of its oxidation peak, and the electrolysis was found to proceed in two steps. The current observed was ca. 9 mA at the beginning of the electrolysis and decayed following a manner of the first-order kinetics.[21] One electron passed per molecule of the complex for ca. 15 min and the current decreased to 1 mA. Then, the current was increased gradually again and approximately two more electrons passed additionally to reach completion of the electrolysis.

Visible and near-infrared absorption spectra were observed after one-electron oxidation of the complexes **1**—**4**. In the region above 500 nm, each oxidized complex (including **4**) gave only one band detected around 625 nm. Since ferricinium cation $[Fe(C_5H_5)_2]^+$ was reported to have a characteristic band of a Ligand (e_{1u})→Fe (e_{2g}(3d)) transition at ca. 620 nm,[22] the band observed was attributable to a similar transition in the (ferrocenylcarbonyl)palladium complexes oxidized. Near-infrared absorption bands for light-induced intervalent electron-transfer were described for some heterobinuclear complexes upon oxidation,[23,24] which involved ferrocenyl groups as one component similarly to our complexes. The electron-transfer bands were expected in the range of 700 to 2000 nm, but such a band was not discernible in the spectra of **1**—**4** after one-electron oxidation.

On the basis of these results, the redox system under consideration was concluded to be the process of Fe(II)$\rightleftarrows$Fe(III) in the ferrocenyl moiety. As for the bulk electrolysis of **4**, the Fe center was oxidized similarly at the first step and then some kinds of oxidative decomposition of the H_2BPz_2 group would occur as the second step. The oxidative decomposition of the H_2BPz_2 group seemed to be associable with some reducing ability of the group, suggested previously.[9,10]

When cyclic voltammograms of **1**—**4** were performed in a wider potential-range, an additional irreversible anodic wave appeared at a potential more than ca. 1300 mV, owing to oxidation of the Pd(II) sites.[23]

Formal redox potentials[18] $E°$ for the Fe(III)/Fe(II) couples of **1**—**4** were more anodic than that of ferrocene, and this was ascribed to electron-withdrawing effects of their palladiocarbonyl structures from the Fe redox centers. The effects of the four kinds of palladiocarbonyl structures were quite comparable. The ordering for the readiness of oxidation of the Fe centers was $\mathbf{4} \geqq \mathbf{3} > \mathbf{2} > \mathbf{1}$. Therefore, electron-withdrawing effects of the [poly(1-pyrazolyl)borato]palladiocarbonyl moieties from the Fe centers were smaller than that of the chloro(triphenylphosphine)palladiocarbonyl moiety. In addition, this parallelism indicated also that the [tetrakis(1-pyrazolyl)borato]-palladium moiety possessed greater ability for withdrawing electrons from the Fe center than the other poly(1-pyrazolyl)borate analogues, possibly owing to its larger electron-delocalization over the pyrazolyl groups.

Experimental

General Procedures and Materials. ^1H- and ^{13}C-NMR spectra were run on JEOL model FX-90-Q (FT type) and MH-100 spectrometers with tetramethylsilane as an internal standard. Temperatures of NMR samples were determined with methanol or 1,3-propanediol. IR spectra were obtained using Hitachi 285 and Shimadzu IR-450 spectrometers. Melting points were observed on a Yanagimoto MP-S3 microstage apparatus in capillary tubes and are uncorrected. Electronic spectra (260—2100 nm) were recorded on a Hitachi 323 UV-VIS-NIR spectrophotometer.

(Chloroformyl)ferrocene[25] and $M[H_nBPz_{4-n}]$ (M=Na and K)[9] were prepared according to the reported methods. Preparative and electrochemical operations were performed under dry nitrogen.

Preparation of $[Pd(COFc)Cl(PPh_3)_2]$ 1. The powder of $[Pd(PPh_3)_4]$ (850 mg) was added in portions to a benzene solution (20 cm^3) of (chloroformyl)ferrocene (230 mg) and the mixture was stirred for 24 h at ambient temperature. The resulting precipitates were collected and washed with diethyl ether. Yellowish orange microcrystals (520 mg) were obtained and characterized as **1**. Vis(CH_3CN) 450 nm (ε 625).

Preparation of $[Pd(COFc)(BPz_4)(PPh_3)]$ 2. A mixture of **1** (218 mg) and $K[BPz_4]$ (95 mg) in dichloromethane (20 cm^3) was stirred overnight. After concentration, the reaction mixture passed through a silica-gel column (200 mesh, 1.2×20 cm) to give a red fraction by eluting with dichloromethane–diethyl ether (2:1). The fraction was evaporated to dryness and the residue was recrystallized from dichloromethane and hexane, affording an orange powder (98 mg) of **2**. Vis(CH_3CN) 464 nm (ε 506).

Preparation of $[Pd(COFc)(HBPz_3)(PPh_3)]$ 3. Complex **1** (200 mg) was treated with $Na[HBPz_3]$ (63 mg) in dichloromethane (20 cm^3). After stirring for 24 h, the solvent was removed in vacuo. Then, the benzene extract was chromatographed on a silica-gel column, and a red fraction eluted by dichloromethane–diethyl ether (4:1) was evaporated to dryness. The resulting solid was recrystallized from diethyl ether and hexane to give orange microcrystals (74 mg) of **3**. Vis(CH_3CN) 464 nm (ε 441).

Preparation of $[Pd(COFc)(H_2BPz_2)(PPh_3)]$ 4. Potassium dihydrobis(1-pyrazolyl)borate $K[H_2BPz_2]$ (50 mg) was mixed with **1** (180 mg) in THF (20 cm^3), followed by stirring for 24 h at room temperature. The solvent was evaporated under reduced pressure and recrystallization of the residue from benzene and diethyl ether gave yellowish orange microcrystals (45 mg) of **4**. Vis(CH_3CN) 461 nm (ε 456).

Reaction of 1 with 1,10-Phenanthroline (phen). 1,10-Phenanthroline monohydrate (58 mg) was added to a benzene suspension (50 cm^3) of **1** (250 mg) and the mixture was stirred for 2 h. After concentration to a small volume, addition of hexane gave orange precipitates (81 mg) of **5**.

Reaction of 1 with 2,2′-Bipyridine (bpy). A mixture of **1** (250 mg) and 2,2′-bipyridine (50 mg) in benzene (50 cm^3) was stirred at ambient temperature for 2 h and the resulting precipitates were collected and washed with diethyl ether to afford pale yellow microcrystals (74 mg) of **6**.

Reaction of 1 with $AgClO_4$ in CH_3CN. An CH_3CN solution (5 cm^3) of $AgClO_4 \cdot H_2O$ (52 mg) was added dropwise to an CH_3CN suspension (20 cm^3) of **1** (200 mg). After stirring of the mixture for 2 h and evaporation under vacuum to dryness, recrystallization of the residue from dichloromethane and diethyl ether yielded pale yellow microcrystals (130 mg), **7**.

Electrochemical Studies. Electrochemical experiments were carried out with a standard three-electrode electric circuit, using a Hokuto Denko HA-301 potentiostat and a HB-104 function generater. Acetonitrile test-solutions (20 cm^3) contained (ferrocenylcarbonyl)palladium complexes (10^{-3} mol dm^{-3}) and (n-$Bu_4N)PF_6$ (0.1 mol dm^{-3}) as the supporting electrolyte. The reference and auxiliary electrodes were separated from the test solution by a tube with glass frits, and the tube contained electrolytic solvent and the supporting electrolyte. Working electrodes were a Pt disc ($3\,\mathrm{mm}^{\phi}$) and gauze (12 cm^2, 80 mesh) for cyclic voltammetry and bulk electrolysis, respectively. The auxiliary electrode was a Pb plate and the reference electrode was a Pt wire in a solution of $[Fe(C_5H_5)_2]$ (0.01 mol dm^{-3}), $[Fe(C_5H_5)_2]PF_6$ (0.01 mol dm^{-3}), and (n-$Bu_4N)PF_6$ (0.1 mol dm^{-3}) in CH_3CN.

Electronic Absorption Spectra of 1—4 after One-electron Oxidation. The complexes **1**—**4** in nitrogen-deaerated acetonitrile solutions (10^{-3} mol dm^{-3}) were served for bulk electrolysis at appropriately controlled potentials. After one-electron oxidation, a syringe was used to transfer ca. 3 cm^3 of the solutions to a 10 mm quartz cuvette under nitrogen, taking care to avoid dilution with solvent in the auxiliary electrode compartment. Electronic absorption bands under consideration were observed within 5 min after completion of the electrolysis.[26] Molar absorptivities ε were evaluated from the absorbances obtained, and were based on the concentration of the complexes charged.

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