Bipyridyl–Metal Complexes. 2.[†] Synthesis and Characterization of Palladium(II) Chloride Complexes of 6-Ferrocenyl-2,2′-bipyridine, 2-Ferrocenyl-1,10-phenanthroline, and 6-Ruthenocenyl-2,2′-bipyridine and the Single-Crystal X-ray Structure of (1,1′-Bis(2,2′-bipyrid-6-yl)ferrocene-*N*,*N*′)palladium Chloride

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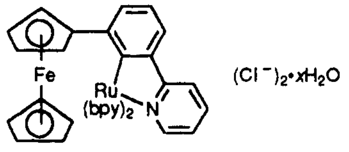
The coordination chemistry of a series of ferrocenyl- and ruthenocenylbipyridines such as 6-ferrocenyl-2,2′-bipyridine (HL1), 1,1′-bis(2,2′-bipyrid-6-yl)ferrocene (HL2), 2-ferrocenyl-1,10-phenanthroline (HL3), and 2-(2,2′-bipyrid-6-yl)-1-((dimethylamino)methyl)ferrocene (HL5) has been studied. The reaction of dichloro(η^4-1,5-cyclooctadienyl)palladium with a series of ferrocenylbipyridine and ferrocenylphenanthroline ligands gives the new complexes [(L1)PdCl], [(L2)PdCl] (L is the anion of HL in which a cyclopentadienyl proton α to the bipyridyl sustituent has been removed; e.g., L1 refers to HL1 with one cyclopentadienyl proton α to the bipyridyl removed and the position palladated), and [(HL3)PdCl$_2$]. The synthesis of the new ligand 2-(2,2′-bipyrid-6-yl)-1-((dimethylamino)methyl)ferrocene (HL5) from the direct reaction of 2-lithio-1-((dimethylamino)methyl)ferrocene with 2,2′-bipyridine is described, in addition to the characterization of 6-ruthenocenyl-2,2′-bipyridine and 2-ruthenocenyl-1,10-phenanthroline. The single-crystal X-ray structure of the violet complex [(L2)PdCl·0.5CH$_2$Cl$_2$] was determined and gave the following structural data: orthorhombic, *Pbca*, a = 13.879 (3) Å, b = 19.329 (3) Å, c = 20.854 (4) Å, V = 5594.4 (18) Å^3, C$_{30}$H$_{21}$ClFeN$_4$Pd·0.5CH$_2$Cl$_2$, Z = 8, ρ_{calc} = 1.612 g cm^{-3}, μ = 1.37 mm^{-1}, R_F = 0.076, R_{wF} = 0.093, GOF = 1.02. Complexes [(L)PdCl] (L = L1, L2) are the first reported examples of a tridentate coordination mode of a bipyridyl ligand containing ferrocene.

Introduction

The chemistry of bipyridyl ligands has been extensively explored over the past two decades or so, since these compounds represent a family of easily accessible, easily modifiable ligands.[1] In addition, they are relatively air stable, in contrast to other commonly used ligands such as tertiary phosphines, which are prone to oxidation. There now exists an enormous literature data base on the complexes of 2,2′-bipyridyl, which has accumulated rapidly following the initial discovery that ruthenium complexes can act as catalysts in the photoinduced water-splitting reaction.[2] The research in the area of water splitting using modified (bipyridyl)ruthenium complexes and the prototype [(bpy)$_3$Ru]$^{2+}$(A$^-$)$_2$ (A = general anion) continues to grow. The work in this area is now focused on overcoming inherent problems of the current catalytic systems used in photoinduced water splitting such as obtaining the physical separation of oxidation and reduction catalytic sites and maintaining the structural integrity of the parent ruthenium complex throughout the catalytic cycle. Although the most studied complexes to date remain those of ruthenium,[3] modified palladium and platinum[4] complexes are now under investigation due to their possible uses in chemotherapy. Our own interest in this area is essentially a synthetic one, in which we are attempting to achieve redox site separation in complexes derived from bipyridyls. In addition, we have recently carried out work on the oligomerization and polymerization of halobipyridines with acetylene using palladium(0) catalysis.[5] In a recent paper, the synthesis of some ferrocenyl-substituted bipyridyls and 1,10-phenanthrolines were described, as well as the cationic ruthenium complex 1, containing the ligand 6-ferrocenyl-2,2′-bipyridine (HL1)[6] (the ligands containing pyridyls, dipyridyls and phenanthrolinyls are designated with the prefix H to represent a proton substituent in the α-position of the cyclopentadienyl ring with respect to the heterocyclic substituent. In complexes where an α-metalation has taken place, the H is therefore omitted). In our ligand design work, we are attempting the preparation of bimetallic complexes in which a second transition metal can be incorporated directly onto the modified ligand and, as such, it becomes necessary to commence with model systems and investigate the coordination of the second transition metal.



1, [(HL1)Ru(bpy)$_2$](Cl$^-$)$_2$·xH$_2$O

In complex 1, the ferrocenylbipyridyl ligand coordinates in the normal bidentate mode; however, in related palladium complexes of ferrocenylpyridine the cyclopentadienyl ring is cyclometalated to give compound 2.[7] Recently,

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[†] Part 1: Reference 6a.

[‡] Work carried out in part at the University of Ottawa and The National Research Council, Ottawa, Ontario, Canada.

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(3) For a leading recent review see: Meyer, T. J. *Acc. Chem. Res.* **1989**, 22, 163 and references therein.

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(6) (a) Butler, I. R.; Roustan, J.-L. *Can. J. Chem.* **1990**, 68, 2212. The complex Re(1)(CO)$_3$Br has also been prepared[6b] as an orange solid. ^{1}H NMR (CDCl$_3$): δ 4.04 (s, 5 H), 4.47 (q, 2 H), 4.97 (t, 2 H), 5.04 (t, 2 H), 7.38 (td, 1 H), 7.83 (t, 1 H), 8.13 (dd, 1 H), 8.03 (asymmetric d, 1 H), 7.90 (t, 1 H overlapped with d, 1 H), 8.98 (dd, 1 H). (b) Butler, I. R.; Tajiq, M. Unpublished results.

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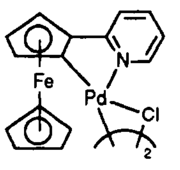

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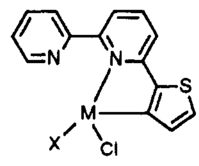

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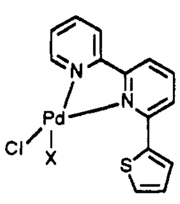

4

M = Pd, Pt; X = Cl, OAc

Constable and co-workers, in an elegant series of papers,[8] have prepared metal complexes of pyridyl-based ligands containing both thienyl and phenyl groups, in which they observe the cyclometalation of the thienyl and phenyl groups by a variety of metals. For example, they have prepared complexes 3 and 4. In our own work, we have observed similar results with 6,6′-bis(2-thienyl)-2,2′-bipyridine on palladium complexation.[9] In this paper I describe the preparation of related complexes of 6-ferrocenyl-2,2′-bipyridine and 2-ferrocenyl-1,10-phenanthroline. In addition, the syntheses of two new ferrocene-based ligands are described, as well as the characterization of the ruthenocenyl analogues of ferrocenylbipyridines.

Experimental Section

The ligands 6-(ferrocenyl)-2,2′-bipyridine (HL1), 1,1′-bis(2,2′-bipyrid-6-yl)ferrocene (HL2), 2-ferrocenyl-1,10-phenanthroline (HL3), and 1,1′-bis(1,10-phenanthrolin-2-yl)ferrocene (HL4) were prepared using the literature procedure.[6] Solvents were predried and freshly distilled prior to use. Ruthenocene was prepared from hydrated ruthenium trichloride and freshly cracked cyclopentadiene using powdered zinc in ethanol at low temperature (−70 °C to room temperature.)[10] Bipyridines and phenanthrolines were obtained from the Aldrich Chemical Co. and were used without further purification. ^{1}H NMR spectra were recorded using a Varian XL-300 spectrometer, in dichloromethane-d_2 or chloroform-*d*, unless otherwise stated; all *J* values are in hertz. Mass spectra were recorded using a VG-Analytical 7070E instrument at the University of Ottawa Mass Spectroscopy Centre. Abbreviations used for NMR data: s = singlet, d = doublet, t = triplet, m = multiplet, a = asymmetric, b = broad, pd = pseudodoublet. Full ^{1}H NMR peak assignments are given where possible. The numbering of the heterocyclic protons follows the numbering scheme for the carbon atoms to which they are attached: this follows the normal conventions for the parent bipyridines by starting with N(1) and proceeding around the ring in the direction in which the carbon atom which links the pyridine rings is of lowest possible number. Chromatographic work was carried out using neutral alumina, activity grade I—the other grades were prepared by addition of the appropriate quantity of water. Elemental analysis data are for samples dried under vacuum for several hours, as there is a tendency for the pyridyl compounds to form partial hydrates, as observed by ^{1}H NMR spectroscopy. In addition, the palladium complexes crystallized as partial solvates from dichloromethane and the analytical data for these crystalline compounds are calculated on the basis of the quantity of dichloromethane observed in individual samples by ^{1}H NMR measurements.

Preparation of 2-(2,2′-Bipyridyl)-1-((dimethylamino)methyl)ferrocene (HL5). The procedure used is similar to that described for the preparation of the unsubstituted ferrocene analogues,[6] on scales ranging from 10 to 100 mmol. A solution of monolithiated 1-((dimethylamino)methyl)ferrocene[11] was prepared by treating 1-((dimethylamino)methyl)ferrocene in diethyl ether with a commercially available 1.6 M *n*-butyllithium solution in hexane (1.1 molar excess). The mixture was stirred at room temperature for 5 h, before a 2-fold excess, with respect to the ferrocenylamine, of 2,2′-bipyridine was added to the cooled (ca −70 °C) solution. The solution was warmed slowly to room temperature and was subsequently stirred for 25 h before being poured into water. The organic phase was extracted with diethyl ether, and the extracts were concentrated to give a deep orange-red oil. The oil was chromatographed on a grade IV neutral alumina column (failure to deactivate the column results in the product adhering strongly to the support). A series of colored fractions were collected, with hexane initially as eluent; then the polarity was gradually increased by incremental addition of diethyl ether and then subsequently dichloromethane. Each fraction was concentrated to dryness to leave an oil, and its ^{1}H NMR spectrum was recorded. Identification of the product-containing bands was made by locating the $N(CH_3)_2$ group at δ ~2.2 in the spectra. The product-containing bands were recombined and rechromatographed to give a deep red-orange oil, which on crystallization (40 h at −20 °C) using a 50/50 mixture of hexane and diethyl ether yielded deep red-black crystals of the product, HL5. Yields ranged from 14 to 20%. In subsequent preparations, the product-containing fractions were located by a TLC comparison with an authentic sample. ^{1}H NMR ($CDCl_3$): δ 2.19 (s, 6 H, $N(CH_3)_2$), 3.33 (d, 1 H, *J* = 13.0, CH_2 a), 4.03 (s, 5 H, unsubstituted C_5H_5), 4.31 (t, 1 H, C_5H_3 a), 4.40 (bs, 1 H, C_5H_3b), 4.41 (d, 1 H, CH_2 b), 4.82 (bt, 1 H, C_5H_3 c) [7.30 (ddd, 1 H), 7.57 (dd, 1 H), 7.70 (t, 1 H), 7.84 (td, 1 H), 8.21 (dd, 1 H), 8.56 (bd, 1 H), 8.67 (ddd, 1 H), bipyridyl protons]. Mass spectrum (*m*/*e* (relative intensity)): parent ion 397 (10.1). Anal. Calcd for $C_{23}H_{23}FeN_3$: C, 69.53; H, 5.84; N, 10.58. Found: C, 69.37; H, 5.57; N, 10.76.

Preparation of HL6, HL7, HL8, and HL9. The ruthenocenyl analogues of HL1, HL2, and HL3 (HL6, HL7, and HL8) were prepared using the literature procedure described for the preparation of HL1, HL2, and HL3[6] by simply replacing ferrocene with ruthenocene. Similarly, the preparation of 6-ferrocenyl-2,2′:6′,2″-terpyridine (HL9) was accomplished using the adapted literature synthesis of HL1, by replacing 2,2′-bipyridine with 2,2′:6′,2″-terpyridine. The characterizations follow.

6-Ruthenocenyl-2,2′-bipyridine (HL6). ^{1}H NMR ($CDCl_3$): δ 4.44 (s, 5 H, C_5H_5), 4.73 (t, 2 H, $J_{H_\alpha-H_\beta}$ = 1.8 Hz, β-C_5H_4), 5.38 (t, 2 H, α-C_5H_4), 7.27 (td, 1 H, $J_{5'-6'}$ = 4.8, $J_{5'-4'}$ = 7.9, $J_{5'-3'}$ = 1.1, H-5′), 7.32 (dd, 1 H, J_{5-4} = 7.8, J_{5-3} = 1.0, H-5), 7.63 (t, 1 H, J_{4-3} = 7.8, H-4), 7.80 (td, 1 H, $J_{4'-3'}$ = 7.9, $J_{4'-6'}$ = 1.8, H-4′), 8.14 (dd, 1 H, H-3), 8.48 (dt, 1 H, $J_{3'-6'}$ = 1.0, H-3′), 8.64 (ddd, 1 H, H-6′). Mass spectrum (*m*/*e* (relative intensity)) 388 (27.0), 387 (10.4), 386 (49.2), 385 (45.1), 383 (36.6), 193 (13.9), 192 (12.3), 157 (10.9), 156 (100). Anal. Calcd for $C_{20}H_{16}N_2Ru$: C, 62.32; H, 4.18; N, 7.27. Found: C, 62.43; H, 4.39; N, 7.46.

1,1′-Bis(2,2′-bipyrid-6-yl)ruthenocene (HL7). ^{1}H NMR ($CDCl_3$): δ 4.75 (t, 4 H, β-C_5H_4), 5.33 (t, 4 H, α-C_5H_4), 6.79 (dd, 1 H, J_{5-4} = 7.8, J_{5-3} = 1.0, H-5), 7.13 (t, 1 H, J_{4-3} = 7.8, H-4), 7.23 (m, 1 H, H-5′), 7.67 (td, 1 H, $J_{4'-3'}$ = 7.9, $J_{4'-6'}$ = 1.5, H-4′), 7.94 (dd, 1 H, H-3), 8.23 (dd, 1 H, $J_{5'-3'} \cong 1.1$, $J_{3'-6'} \cong 1.2$, H-3′), 8.61 (m, 1 H, H-6′). Mass spectrum (*m*/*e* (relative intensity)): 543 (14.5), 542 (56.4), 541 (7.9), 537 (100.0), 385 (19.1), 384 (11.5), 383 (10.3), 295 (10.2), 215 (12.7). Anal. Calcd for $C_{30}H_{22}N_4Ru$: C, 66.78; H, 4.11; N, 10.38. Found: C, 66.82; H, 4.32; N, 10.16.

2-Ruthenocenyl-1,10-phenanthroline (HL8). ^{1}H NMR ($CDCl_3$): δ 4.45 (s, 5 H, C_5H_5), 4.79 (t, 2 H, $J_{\alpha-\beta}$ = 1.7 Hz, β-C_5H_4), 5.56 (t, 2 H, α-C_5H_4), 7.58 (dd, 1 H, J_{8-7} = 8.1, J_{8-9} = 4.4, H-8), 7.68 (d, 1 H, J_{3-4} = 8.4, H-3), 7.71 (s, 2 H, H-5, H-6), 8.03 (d, 1 H, H-4), 8.20 (dd, 1 H, J_{7-9} = 1.7, H-7), 9.18 (dd, 1 H, H-9). Mass spectrum (*m*/*e* (relative intensity)): 412 (23.5), 411 (19.7), 410 (47.5), 409 (50.8), 408 (40.4), 407 (29.0), 406 (16.4), 404 (6.0), 205

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(3.8), 180 (11.5). Anal. Calcd for $C_{22}H_{16}N_2Ru$: C, 64.54; H, 3.94; N, 6.84. Found: C, 64.62; H, 4.04; N, 6.92.

6-Ferrocenyl-2,2′:6′,2″-terpyridine (HL9). ^{1}H NMR ($CDCl_3$): δ 4.05 (s, 5 H, C_5H_5), 4.41 (t, 2 H, $J_{\alpha-\beta}$ = 1.9 Hz, β-C_5H_4), 5.03 (t, 2 H, α-C_5H_4), 7.32 (ddd, 1 H, $J_{5''-6''}$ = 4.8 Hz, $J_{5''-4''}$ = 7.5, $J_{5''-3''}$ $\approx$ 0.7, H-5″), 7.43 (dd, 1 H, J_{5-4} = 7.8, J_{5-3} = 0.9, H-5), 7.73 (t, 1 H, J_{4-3} = 7.8, H-4), 7.86 (td, 1 H, $J_{4''-6''}$ = 19.4, H-4″), 7.97 (t, 1 H, $J_{4'-3'}$ = $J_{4'-5'}$ = 7.8, H-4′), 8.41 (dd, 1 H, H-3), 8.45 (dd, 1 H, H-3″), 8.60 (ddd, 1 H, H-5′*), 8.61 (dd, 1 H, H-3′*), 8.69 (ddd, 1 H, $J_{6''-3''}$ = 0.9, H-6″) (asterisks denote tentative assignments). Mass spectrum (*m*/*e* (relative intensity)): 418 (25.3), 417 (86.2), 416 (26.2), 353 (19.4), 352 (74.1), 351 (70.3), 350 (31.6), 324 (10.4), 323 (14.3), 296 (10.1), 234 (21.1), 233 (100.0), 232 (42.3), 205 (22.4). Anal. Calcd for $C_{25}H_{19}FeN_3$: C, 71.96; H, 4.59; N, 10.07. Found: C, 71.86; H, 4.64; N, 9.97.

1-(Diphenylphosphino)-2-(2-pyridyl)ferrocene (PPh_2L10).[12] A solution of 2-pyridylferrocene (2.63 g, 10 mmol) in diethyl ether (15 mL) was treated with 5 mL of a 2.0 M solution of *n*-butyllithium. After it was stirred for 6 h, the solution was cooled to ca. −70 °C and chlorodiphenylphosphine (2.20, 10 mmol) was slowly added. The mixture was warmed slowly to room temperature and was stirred for 5 h. Following hydrolysis (H_2O, 10 mL) the organic phase was separated, dried over anhydrous $MgSO_4$, and concentrated. The mixture was chromatographed on a neutral alumina support (Grade II), with diethyl ether as eluent. Collection of the major orange fraction, concentration, and crystallization from hexane/diethyl ether gave 1-(diphenylphosphino)-2-(2-pyridyl)ferrocene (35%). The reaction was repeated with the reduced lithiation time of 50 min, using an identical workup procedure, and the product yield was increased to 65%. ^{1}H NMR ($CDCl_3$): δ 3.73 (ddd, 1 H, H_α (to P)), 4.03 (s, 5 H, C_5H_5), 4.43 (td, 1 H, $J_{\alpha-\beta}$ = 2.5 Hz, J_{P-H} = 0.6 Hz, H β (to P) C_5H_3), 5.10 (ddd, 1 H, J_{P-H} = 1.4, $J_{\gamma-\alpha}$ = 1.4, H γ (to P) C_5H_3), 6.96 (ddd, 1 H, pyridyl H-4), 7.10–7.57 (m's, 11 H), 7.76 (dd, 1 H), 8.32 (ddd, 1 H, pyridyl H-6). Mass spectrum (m/e (relative intensity)): 448 (21.2), 447 (68.2, $M^{\bullet+}$), 371 (26.5), 370 (19.0), 248 (9.7), 172 (29.9). Anal. Calcd for $C_{27}H_{22}FeNP$: C, 72.50; H, 4.96; N, 3.13. Found: C, 72.84; H, 5.23; N, 2.97. The phosphine oxide of the title compound was a byproduct. Mass spectrum (*m*/*e* (relative intensity)): 464 (31.2), 463 (100.0, $M^{\bullet+}$), 399 (19.1), 398 (69.4), 274 (26.1), 264 (11.3), 263 (48.9), 218 (12.7).

(2-Pyridylphenylphosphino)ferrocene (L11). The title compound was prepared by the ring cleavage of 1,1′-ferrocenediylphenylphosphine[13] with 2-lithiopyridine, which was generated in situ at −78 °C from 2-bromopyridine and *n*-butyllithium using well-established procedures. The product was isolated as a yellow-orange crystalline solid. Yields range from 25 to 45%. ^{1}H NMR ($CDCl_3$): δ 4.04 (m, 1 H, β-C_5H_4), 4.06 (s, 5 H, C_5H_5), 4.35 (m, 1 H, β-C_5H_4), 4.38 (m, 1 H, α-C_5H_4), 4.44 (m, 1 H, α-C_5H_4), 7.28 (ddd*, pyridyl H-5), 7.32 (dd*, 1 H), 7.33–7.55 (m's, 7 H), 8.69 (dd, 1 H, pyridyl H-6). (Asterisks denote that the positions change depending on solvent concentration). Mass spectrum (*m*/*e* (relative intensity)): 373 (21.3), 372 (98.8), 371 (100.0, $M^{\bullet+}$), 306 (19.3), 186 (21.9). Anal. Calcd for $C_{21}H_{18}FeNP$: C, 67.95; H, 4.89; N, 3.77. Found: C, 67.83; H, 5.00; N, 3.98.

Other byproducts isolated include the known (*n*-butylphenylphosphino)ferrocene[14] and the phosphine oxide of the title compound, (2-pyridyl)phenylferrocenylphosphine oxide: ^{1}H NMR δ 4.03 (s, 5 H), 4.06 (m, 1 H), 4.44 (m, 1 H), 4.62 (m, 1 H), 4.74 (m, 1 H), 7.35–7.55 (m's, 5 H), 7.76 (bt, 1 H), 7.88 (ddd, 1 H), 8.29 (td, 1 H), 8.76 (dd, 1 H). Mass spectrum (*m*/*e* (relative intensity)): parent ion 389 (100.0).

1-(2-Pyridyl)-1′-(diphenylphosphino)ferrocene (HL12). A solution of 1-lithio-1′-(diphenylphosphino)ferrocene[13] was prepared in situ from ferrocenediylphenylphosphine (1.46 g, 5 mmol) and phenyllithium (10 mmol, 2.0 M solution in diethyl ether) in diethyl ether at −70 °C. The yellow product solution was treated with excess pyridine (5 mL) and stirred for 24 h. After hydrolysis, the product was obtained by column chromatography in low yield (ca. ~10%) as an orange oil which solidified on drying under vacuum. ^{1}H NMR ($CDCl_3$): δ 3.93 (pq, 2 H, $J_{H_{\alpha 1}-H_{\beta 1}}$ = 1.7 Hz, $J_{P-H\alpha}$ $\cong$ 1.0, $H_\alpha C_5H_4$) [4.33], 4.19 (bt, 2 H, $H_{\beta 1}$ C_5H_4) [4.52], 4.24 (t, 2 H, $H_{\beta 2}$ C_5H_4) [4.38], 4.81 (t, 2 H, $H_{\beta 2}$ C_5H_4) [4.97] (figures in brackets refer to positions of peaks due to the phosphine oxide derivative; α1 refers to P substituted cyclopentadienyl ring), 7.04 (ddd, 1 H, pyridyl H-5), 7.24–7.42 (m's, 11 H), 7.97 (dd, 1 H), 8.44 (ddd, 1 H, pyridyl H-6). Mass spectrum (*m*/*e* (relative intensity)): 448 (50.7), 447 (100.0, $M^{\bullet+}$), 446 (83.8), 387 (10.4), 370 (15.1), 263 (4.9). Anal. Calcd for $C_{27}H_{22}FeNP$: C, 72.50; H, 4.96; N, 3.13. Found: C, 72.42; H, 4.88; N, 3.23.

Reaction of 2-Lithio-1-(2-pyridyl)ferrocene with Bipyridine. (a) A solution of 2-lithio-1-(2-pyridyl)ferrocene was prepared from 2.63 g (10 mmol) of 2-pyridylferrocene[15] and 5 mL of a 2.0 M solution of *n*-butyllithium in diethyl ether. After the mixture was stirred for 10 h, an excess of 2,2′-bipyridine was added to give a deep red-violet solution. The mixture was stirred for a further 20 h before hydrolysis with H_2O (20 mL). The organic layer was separated, and the aqueous layer and solids were further extracted with dichloromethane. The organic layer was dried over $MgSO_4$ and filtered. At this stage, a TLC examination of the product mixture was undertaken, which showed large quantities of (6-*n*-butyl-2-pyridyl)ferrocene[12] and (2-pyridyl)ferrocene and only small amounts of eight other slower moving colored bands, which were assigned to bipyridyl-containing fractions.

(b) The reaction was repeated as described above; however, the solution was stirred for 50 min before addition of 2,2′-bipyridine. After the mixture was stirred for a further 10 h, TLC (20% diethyl ether/80% hexane eluent mixture) indicated the presence of three major products: (a) (6-*n*-butyl-2-pyridylferrocene),[12] (b) 2-pyridylferrocene, and (c) two slow-moving bands, identified by mass spectroscopy as containing 2,2′-bipyridine. After extractions and drying of the product solution as described above, the solution volume was reduced to a few milliliters to give a red-black oil. The mixture was then chromatographed on a neutral alumina grade V column (eluent hexane initially, followed by diethyl ether and finally ethyl acetate). Even using a fully deactivated column, substantial product decomposition was apparent. The fractions containing bipyridine were isolated and taken to dryness again to give an oil. Attempts at recrystallization were not successful, and no pure sample of 2-(2,2′-bipyrid-6-yl)-1-(2-pyridyl)ferrocene (L13), was obtained. Mass spectroscopy did, however, show the parent ion to be present, indicating that the product was present in the sample: parent ion *m*/*e* 412.

Preparation of Palladium Complexes: General Procedure. A mixture of the appropriate ligand HL1, HL2, HL3, or HL5 (1.5 molar excess) in dichloromethane and (1,5-cyclooctadienyl)palladium dichloride was stirred for 20 h. The solution volume was reduced to a few milliliters, and the product was precipitated by incremental addition of hexane. The powdered product was quickly redissolved in the minimum quantity of dichloromethane, and a top layer of an equal volume of diethyl ether was added carefully. After 2–3 days, the products were obtained as deep red-violet solids. All are crystalline with the exception of the product from HL5, which is obtained as a powder. The yields are between 85 and 95%. N.B.: The crystalline compounds are difficult to redissolve in the solvent from which they were originally crystallized.

Pd[L1]Cl. ^{1}H NMR ($CDCl_3$): δ 4.18 (broad s, 5 H), 4.58 (bt, 1 H), 4.66 (bs, 1 H), 4.93 (bs, 1 H), 7.20 (m, 1 H), 7.52 (2 m, 2 H), 7.72 (m, 1 H), 7.84–8.00 (2 m, 2 H), 8.87 (d, 1 H). Anal. Calcd for $C_{20}H_{15}ClFeN_2Pd\cdot 0.2CH_2Cl_2$: C, 48.72; H, 3.12; N, 5.62; Cl, 9.97. Found: C, 48.54; H, 3.08; N, 5.36; Cl, 9.87. The solvent of crystallization was lost on drying the sample.

Pd[L2]Cl. ^{1}H NMR ($CDCl_3$): δ 4.35 (ddd, 1 H), 4.91 (ddd, 1 H), 5.48 (ddd, 1 H), 4.47 (ddd, 1 H, C_5H_4), 4.46 (t, 1 H), 4.59 (dd, 1 H), 4.86 (dd, 1 H, C_5H_3), 5.28 (s, 1 H, CH_2Cl_2), 6.79 (dd,

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1 H), 6.97–7.01 (m's, 3 H), 7.20 (ddd, 1 H), 7.37 (dd, 1 H), 7.78 (dd, 1 H), 7.46 (dd, 1 H), 7.58 (td, 1 H), 7.74 (dd, 1 H), 7.81 (td, 1 H), 8.16 (dd, 1 H), 8.57 (ddd, 1 H), 8.72 (dd, 1 H), bipyridyl protons. Anal. Calcd for $C_{30}H_{21}ClFeN_4Pd{\cdot}0.5CH_2Cl_2$: C, 54.06; H, 3.28; N, 8.27. Found: C, 54.17; H, 3.31; N, 8.42.

Pd[HL3]Cl$_2$. ^{1}H NMR (CD_2Cl_2): 3.95 (s, 5 H, C_5H_5), 4.37 (bs, 2 H), 5.43 (bs, 2 H, C_5H_4), 5.28 (s, 2 H, CH_2Cl_2), 7.76 (dd, 1 H), 7.88 (s, 2 H), 7.98 (d, 1 H), 8.28 (d, 1 H), 8.52 (d, 1 H), 9.34 (d, 1 H), phenanthroinyl protons. Anal. Calcd for $C_{22}H_{16}Cl_2FeN_2Pd{\cdot}CH_2Cl_2$: C, 44.10; H, 2.90; N, 4.47. Found: C, 44.43, H, 2.92, N, 4.48.

Reaction of Pd(1,5-COD)Cl$_2$ with HL5. The reaction of HL5 with Pd(1,5-COD)Cl$_2$ was carried out using the general procedure; however, on crystallization it was found that a mixture of products was obtained from the reaction. Attempted recrystallization from a range of solvents failed to give pure samples. The following data refer to the original mixture of isomers obtained.

Pd[L5]Cl, Pd[HL5]Cl$_2$ (Isomer Mixture). ^{1}H NMR: δ 2.01, 2.21, 2.31, 2.41, 2.51, 2.52, 2.71 (s's, $N(CH_3)$'s), 3.64 (m's, 3 CH_2's), 4.08, 4.12 (s's, C_5H_5's), 4.52, 4.62, 4.68, 4.74, 4.76, 5.40 (m's, C_5H_3), 7.18, 7.36, 7.58, 7.70, 7.75–7.90 (series of multiplets), 8.10, 8.21, 8.64, 8.81, 9.38 (dd, bipyridyl proton resonances). Anal. Calcd for $C_{23}H_{23}Cl_2FeN_3Pd{\cdot}CH_2Cl_2$: C, 43.72; H, 3.79; N, 6.37. Found (two samples): C, 43.03, 44.14; H, 4.15, 4.23; N, 6.34, 6.31.

Pd[L6]Cl and Pd[HL6]Cl$_2$: Reaction of 6-Ruthenocenyl-2,2′-bipyridine with (η^4-1,5-Cyclooctadienyl)palladium Dichloride. To a small sample of 6-ruthenocenyl-2,2′-bipyridine (100 mg, 0.26 mmol) in dichloromethane (5 mL) was added an excess of (η^4-1,5-cyclooctadienyl)palladium dichloride (100 mg, 0.35 mmol). The solution was stirred overnight. Following filtration, the solution was layered with an equal volume of diethyl ether. Slow diffusion of the two layers gave a mixture of crystalline material. Washing with chloroform (5 mL) removed the excess (1,5-COD)PdCl$_2$. The remaining precipitate contained orange and orange-red crystalline material. The orange crystals were observed to be more soluble in chloroform.

(a) Pd[HL6]Cl$_2$: orange, (6-ruthenocenyl-2,2′-bipyridyl-*N*,*N*′)palladium dichloride. ^{1}H NMR ($CDCl_3$): δ 4.39 (s, 5 H, C_5H_5), 4.84 (t, 2 H, β-C_5H_4), 5.60 (t, 2 H, α-C_5H_4), 7.43 (ddd, 1 H, H-5′), 7.59 (dd, 1 H, H-5), 7.69 (td, 1 H, H-4′) 7.71 (t, 1 H, H-4), 7.97 (dd, 1 H, H-3), 8.03 (dd, 1 H, H-3′), 9.22 (ddd, 1 H, H-6′).

(b) Pd[L6]Cl: red-orange, (6-ruthenocenyl-2,2′-bipyridyl-*N*,*N*′)palladium chloride. ^{1}H NMR ($CDCl_3$): δ 4.54 (s, 5 H, C_5H_5), 4.73 (t, 1 H, C_5H_3, H β to Pd), 5.02 (pd, 1 H, C_5H_3, H α to Pd), 5.09 (pd, 1 H, C_5H_3, H γ to Pd), 7.21 (ddd, 1 H), 7.40–8.18 (series of m's, 5 H), 8.87 (ddd, 1 H, H-6′).

Pd[HL8]Cl$_2$: (2-ruthenocenyl-1,10-phenanthrolinyl-*N*,*N*′)-palladium dichloride. ^{1}H NMR ($CDCl_3$): δ 4.73 (s, 5 H, C_5H_5), 4.93 (t, 2 H, $J_{\alpha-\beta}$ = 1.8 Hz, β-C_5H_4), 5.76 (t, 2 H, α-C_5H_4), 7.74 (dd, 1 H, J_{8-9} = 5.3, J_{8-7} = 8.3, H-8), 7.85, 7.88 (2 ad's, 2 H, J_{5-6} = 7.1, H-5, H-6), 7.86 (d, 1 H, J_{3-4} = 7.5, H-3), 8.07 (d, 1 H, H-4), 8.48 (dd, 1 H, J_{7-9} = 1.4, H-7), 9.52 (dd, 1 H, H-9). Anal. Calcd for $C_{22}H_{16}Cl_2NPdRu{\cdot}CH_2Cl_2$: C, 41.12; H, 2.70; N, 4.17. Found: C, 41.32; H, 2.81; N, 4.25.

Pd[HL9]Cl$_2$. A mixture of 6-ferrocenyl-2,2′:6′,2″-terpyridyl (1.0 g, 2.39 mmol) and Pd(1,5-COD)Cl$_2$ (0.7 g, 2.4 mmol) in dichloromethane (10 mL) was stirred overnight under a nitrogen atmosphere. The resultant deep purple solution was treated with 15 mL of diethyl ether to precipitate the product mixture. The precipitate was washed in turn with diethyl ether (10 mL), dichloromethane (20 mL), and methanol (20 mL). A deep black residue remained. The purple solution from the washings was evaporated to dryness and redissolved in dichloromethane; this solution was filtered and a top layer of diethyl ether added. The yield of deep purple microcrystalline Pd[HL9]Cl$_2$ was 22%. The black precipitate was insoluble in ethanol and acetone. Washing with DMF dissolved a small amount of material; however, the solution turned yellow on standing in air. ^{1}H NMR (CD_2Cl_2): δ 4.06 (s, 5 H, C_5H_5), 4.55 (bs, 2 H, β-C_5H_4), 5.14 (bs, 2 H, α-C_5H_4), 7.64 (ddd, 1 H), 7.86–8.06 (m's, 3 H), 8.24 (m, 2 H), 8.51 (dd, 1 H), 8.60–8.80 (2 m's, 2 H), 9.03 (d, 1 H). Anal. Calcd for $C_{25}H_{19}Cl_2FeN_3Pd{\cdot}CH_2Cl_2$: C, 45.96; H, 3.12; N, 6.18; Found: C, 46.32; H, 3.48; N, 6.35. Anal. Found for black insoluble byproduct: C, 34.42; H, 2.81; N, 7.07.

Pd[PPh$_2$L10]Cl$_2$. ^{1}H NMR: δ 4.20 (dd, 1 H), 4.75 (dd, 1 H), 4.88 (s, 5 H), 5.04 (dd, 1 H), 7.07 (td, 1 H), 7.22–7.55 (series of m's, 13 H), 9.37 (d, 1 H). The synthesis as described above for ligands HL1–5. Anal. Calcd for $C_{27}H_{22}Cl_2FeNPPd{\cdot}0.5CH_2Cl_2$: C, 49.51; H, 3.47; N, 2.10. Found: C, 49.60; H, 3.55; N, 2.19.

Reaction of (1,5-COD)PdCl$_2$ with 2-Ferrocenyl-4,4′-bipyridine. The reaction of 2-ferrocenyl-4,4′-bipyridine with (1,5-COD)PdCl$_2$ was carried out on a 10-mmol scale using a procedure identical to the previous preparations. The product precipitated as a deep red-black solid which could not be crystallized due to its insolubility in a large range of organic solvents (acetone, dichloromethane, acetonitrile, methanol). Mass spectrum (*m*/*e* (relative intensity)): 665 (3.9), 544 (2.6), 531 (13.9), 530 (25.9), 529 (51.3), 452 (12.4), 451 (30.5).

Reaction of *n*-Butyllithium with 6-Ferrocenyl-2,2′-bipyridine. To a solution of 6-ferrocenyl-2,2′-bipyridine (3.4 g, 10 mmol) in diethyl ether (30 mL) was added 7.5 mL of a 2.0 M solution of *n*-butyllithium in hexane. After it was stirred for 20 h, the reaction mixture was quenched with D_2O (5.0 mL). The ether layer was separated and dried over anhydrous $CaCl_2$. The filtered solution was reduced in volume to a few milliliters and chromatographed on a short (~12 cm) neutral alumina column to give two orange fractions. Each of these was dried by pumping under vacuum to give, in each case, an oily solid which was examined using ^{1}H NMR spectroscopy and mass spectroscopy. Fraction 1: ^{1}H NMR ($CDCl_3$) δ 0.96–1.92 (series of multiplets), 2.83 (t, *J* = 6 Hz), 2.87 (t, *J* = 6 Hz), 4.02 (s), 4.03 (s), 4.37 (t, $J_{\alpha-\beta}$ = 1.7 Hz), 4.39 (pd), 5.00 (t, *J* = 1.7) (ratio integration signals at δ 5.00:4.39 1:1.4), 7.13 (pt (dd), *J* = 7.9, 0.7), 7.38 (d, *J* = 7.8), 7.65–7.74 (m's including triplet at 7.71 (*J* = 7.7), td at 7.68 (*J* = 7.8, 1.6), and t at 7.70 (*J* = 7.7)), 8.20 (dd, *J* = 7.9, 0.9), 8.24 (dd, *J* = 7.7, 0.9), 8.33 (dd, *J* = 7.7, 0.7). Mass spectrum (*m*/*e* (relative intensity)): parent peaks at 454 (456 (13.4), 455 (38.9), 454 (53.0), 452 (46.6)), $C_{28}H_{30}D_2FeN_2$; 397 (400 (33.3), 399 (99.6), 398 (51.9), 397 (100.0), 396.5 (36.2)), $C_{24}H_{23}DFeN_2$. Fraction 2: ^{1}H NMR ($CDCl_3$) δ 0.64–1.92 (series of m's), 2.64–2.85 (3 t's), 3.89 (d), 3.98 (s), 4.00 (s), 4.02 (s), 4.03 (s), 4.10 (s), 4.38 (d), 4.45 (t), 5.00 (t), 6.42 (d, *J* = 10.3 Hz), 6.97 (dd), 7.13 (dd), 7.37 (dd), 7.39–7.75 (m's including 3 t's), 8.03 (d), 8.25 (d), 8.35 (d). Mass spectrum (*m*/*e* (relative intensity)): 471 (26.1), 470 (45.3), 468 (31.7), $C_{28}H_{30}D_2FeON_2$; 416 (15.5), 415 (25.2), 413 (62.2), 412 (22.0), $C_{24}H_{23}DFeON_2$; 404 (16.0), 399 (20.4), 398 (47.5), 397 (54.7), $C_{24}H_{23}DFeN_2$.

Data for X-ray Analysis of Pd[L2]Cl·0.5CH$_2$Cl$_2$, C$_{30}$H$_{21}$ClFeN$_4$Pd·0.5CH$_2$Cl$_2$. A deep violet crystal of the title complex, measuring approximately 0.40 × 0.40 × 0.40 mm, was selected and mounted on a glass fiber. The following data were obtained: orthorhombic, *Pbca*, *a* = 13.879 (3) Å, *b* = 19.329 (3) Å, *c* = 20.854 (4) Å, V 5594.4 Å^3, $C_{30}H_{21}ClFeN_4Pd{\cdot}0.5CH_2Cl_2$, *Z* = 8, ρ_{calc} = 1.612 g cm^{-3}, μ = 1.37 mm^{-1} (Mo Kα; λ_{α_1} = 0.709 30 Å).

The diffraction intensities of a deep violet crystal were collected using graphite-monochromatized Mo Kα radiation, using the ω-scan mode to $2\theta_{max}$ = 49.9° on an Enraf-Nonius CAD-4 diffractometer, in a thermostated environment (24 ± 1° C). Data were collected in the octants with *hkl* ranges 0–14, 0–20, and 0–22 with equivalents 0 to −14, 0 to −20, and 0 to −22. Of the total of 7173 reflections measured, 4649 were unique, from which 2431 reflections had $I_{net} > 2.5\sigma(I_{net})$. No correction was made for absorption. The cell parameters were obtained following the least-squares refinement of the setting angles using 25 reflections with 2θ between 40 and 50°. The structure was solved by direct methods using the NRCVAX series of programs[15,16] and refined by full-matrix least-squares methods to final residuals of $R_F = 0.076$, $R_{wF} = 0.093$ for significant data and $R_F = 0.142$, $R_{wF} = 0.134$ for all data, where $R_F = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$, $R_{wF} = [\Sigma(w(|F_o|-|F_c|)^2/\Sigma(wF_o^2)]^{1/2}$ and GOF = 1.02 where GOF = $\Sigma[w(|F_o| - |F_c|)^2)/(\text{no. of reflections} - \text{no. of parameters})]^{1/2}$. The merging *R* value for equivalent data, R_m, was 0.082. No significant decay was detected in the standards; however, the data were rather unstable, which may be attributed to the disorder of the solvent molecule. All hydrogen atoms were placed in calculated positions at a distance of 1.08 Å from carbon with their thermal parameters calculated from U_{iso} + 0.01 with respect to their attached carbon atom. Scattering factors were taken from ref 17. The final atomic

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Table I. Atomic Parameters for Non-Hydrogen Atoms[a]

	x	y	z	B_{iso}, Å^2
Pd	0.91950 (10)	0.09986 (7)	0.07065 (8)	3.73 (6)
Fe	0.67529 (18)	0.14032 (13)	0.03890 (15)	3.53 (13)
Cl(1)	0.9800 (4)	0.2025 (3)	0.1101 (3)	5.7 (3)
Cl(2)	0.3383 (9)	0.2308 (6)	0.1548 (7)	6.3 (6)
Cl(3)	0.3779 (13)	0.1047 (7)	0.2174 (8)	9.7 (9)
N(1)	0.8710 (10)	0.0109 (7)	0.0341 (8)	3.5 (7)
N(2)	1.0110 (11)	0.0263 (8)	0.1192 (8)	4.0 (8)
N(3)	0.6970 (10)	−0.0175 (8)	0.1514 (7)	3.4 (7)
N(4)	0.7995 (13)	−0.1758 (10)	0.2158 (9)	5.8 (10)
C(1)	0.9141 (15)	−0.0483 (10)	0.0540 (10)	4.2 (10)
C(2)	0.8818 (17)	−0.1101 (11)	0.0269 (12)	5.2 (11)
C(3)	0.8071 (17)	−0.1094 (10)	−0.0171 (12)	5.3 (12)
C(4)	0.7621 (14)	−0.0475 (10)	−0.0349 (10)	4.4 (10)
C(5)	0.7985 (13)	0.0141 (10)	−0.0067 (10)	3.7 (9)
C(6)	0.9928 (14)	−0.0386 (11)	0.0983 (10)	4.3 (10)
C(7)	1.0502 (16)	−0.0934 (12)	0.1232 (12)	5.5 (11)
C(8)	1.1179 (17)	−0.0795 (14)	0.1646 (14)	6.1 (13)
C(9)	1.1342 (16)	−0.0127 (16)	0.1868 (13)	6.4 (14)
C(10)	1.0794 (16)	0.0411 (11)	0.1619 (11)	5.1 (11)
C(11)	0.7123 (13)	−0.0884 (11)	0.1577 (9)	3.9 (9)
C(12)	0.6552 (15)	−0.1350 (10)	0.1241 (11)	4.7 (10)
C(13)	0.5827 (15)	−0.1129 (9)	0.0858 (11)	4.6 (10)
C(14)	0.5685 (13)	−0.0453 (10)	0.0792 (11)	4.5 (10)
C(15)	0.6282 (13)	0.0024 (10)	0.1120 (9)	3.4 (9)
C(16)	0.7922 (12)	−0.1098 (12)	0.2019 (9)	3.9 (10)
C(17)	0.8543 (15)	−0.0626 (12)	0.2277 (10)	4.7 (10)
C(18)	0.9220 (16)	−0.0847 (13)	0.2713 (11)	5.5 (12)
C(19)	0.9245 (18)	−0.1534 (15)	0.2856 (13)	6.5 (14)
C(20)	0.8637 (18)	−0.1978 (13)	0.2566 (12)	5.9 (12)
C(21)	0.7662 (13)	0.0853 (9)	−0.0185 (9)	3.5 (9)
C(22)	0.8217 (13)	0.1374 (9)	0.0151 (9)	3.6 (9)
C(23)	0.7774 (15)	0.2001 (10)	−0.0056 (11)	4.6 (11)
C(24)	0.6986 (13)	0.1865 (12)	−0.0465 (12)	5.3 (12)
C(25)	0.6915 (13)	0.1147 (11)	−0.0564 (11)	4.8 (11)
C(26)	0.6129 (13)	0.0797 (9)	0.1066 (11)	4.0 (10)
C(27)	0.6678 (14)	0.1308 (10)	0.1368 (11)	4.9 (11)
C(28)	0.6348 (16)	0.1933 (11)	0.1189 (13)	5.4 (12)
C(29)	0.5564 (14)	0.1852 (10)	0.0772 (13)	5.2 (11)
C(30)	0.5408 (13)	0.1123 (10)	0.0694 (12)	5.1 (11)
C(31)	0.394 (3)	0.188 (3)	0.2170 (23)	8.3 (33)

[a] Esd's refer to the last significant digit.

positional parameters and equivalent isotropic temperature factors are listed in Table I, and selected bond and angle data are given in Table II. Final thermal parameters and observed and calculated structure factors are given in Tables III and IV, which are deposited as supplementary material. An ORTEP drawing of [Pd(L2)Cl] is shown in Figure 3. The last cycle was calculated with 63 atoms, 362 parameters, and 2431 reflections using unit weights. The maximum $\Delta:\sigma$ was 0.091. The deepest hole was -2.210 e Å^{-3} and the highest peak 2.540 e Å^{-3}. The highest peaks in the final Fourier difference maps were observed ~1.13 and 1.17 Å from Pd in the z axis, assuming the square-planar ligand environment to be in the xy plane.

Results and Discussion

Our continuing interest concerning the chemistry of ferrocenylbipyridyl compounds, in relation to their potential use as ligands in a variety of applications, led us to prepare some ruthenocenyl analogues and, in addition, to develop some of their coordination chemistry. In this, the second in a series of papers, we describe the synthesis of some palladium complexes derived from these compounds.

6-Ruthenocenyl-2,2′-bipyridine, 2-ruthenocenyl-1,10-phenanthroline, and 1,1′-bis(2,2′-bipyridyl-6-yl)ruthenocene were prepared directly from lithioruthenocenes and the appropriate heterocyclic base, using a procedure identical to the literature method previously applied to the synthesis of the ferrocenyl analogues.[6,18] Isolation of the pure colorless compounds was made following column chromatography. Representative ^{1}H NMR spectra are indicated in Figures 1 and 2. Dry samples of the ferrocenyl analogues have been stored in air for over 3 years with only minor decomposition (darkening observed).

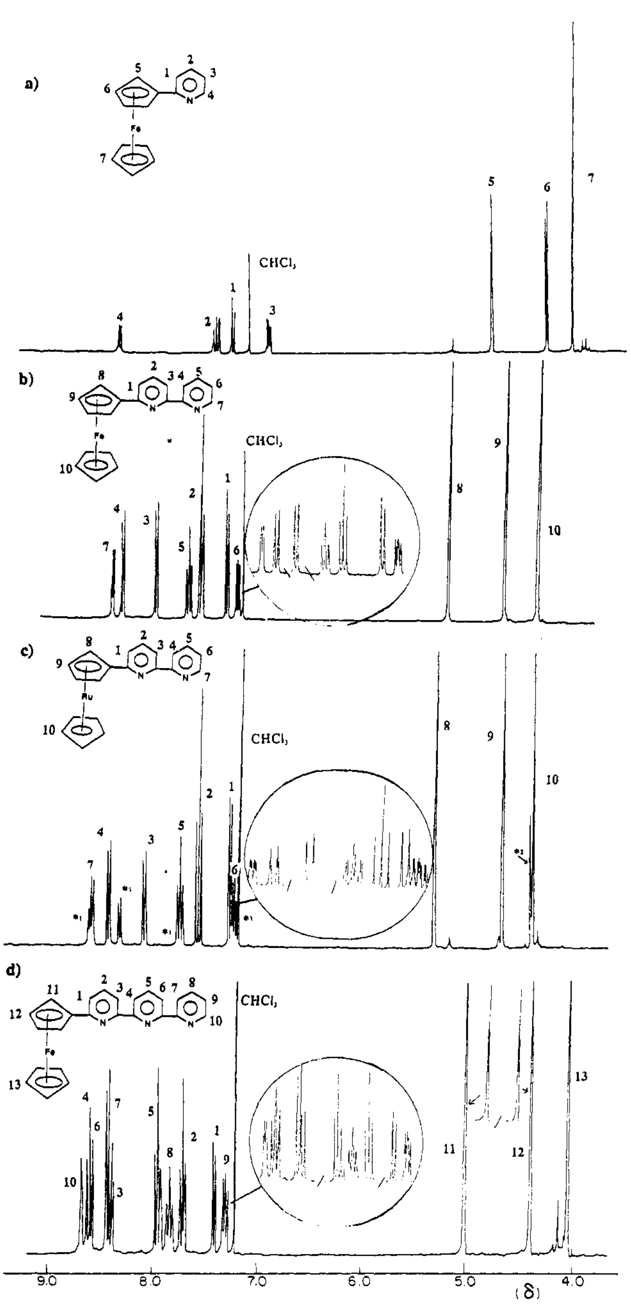

Figure 1. ^{1}H NMR spectral comparison of chemical shifts of (a) 2-pyridylferrocene, (b) 6-ferrocenyl-2,2′-bipyridine (HL1), (c) 6-ruthenocenyl-2,2′-bipyridine (HL6) (2,2′-bipyridyl (*1) and ruthenocene (*2) are present as impurities), and (d) 6-ferrocenyl-2,2′:6′,2″-terpyridine (HL9). N.B.: The reduced figures do not show the small couplings of the ferrocenyl protons; therefore, peaks described as triplets in the text may appear as broad singlets in the reduced figures. The insets show scale-expanded resonances of the spectra. A simplified proton numbering scheme has been adopted.

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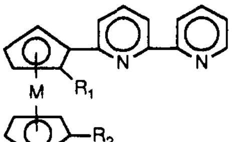
(17) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

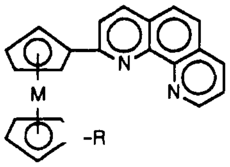
(18) In addition to the synthesis of 1 in the reaction of 2,2′-bipyridine with lithioferrocene, it is possible to adapt the procedure by changing the stoichiometry to prepare the disubstituted derivative bis-6,6′-diferrocenyl-2,2′-bipyridine. ^{1}H NMR (CDCl$_3$): δ 4.42 (t, 4 H), 5.02 (t, 4 H), (s, 10 H), 7.42 (dd, 2 H), 7.73 (t, 2 H), 8.36 (dd, 2 H). Anal. Calcd for $C_{30}H_{24}Fe_2N_2$: C, 68.74, H, 4.61, N. 5.34. Found: C, 68.71; H, 4.55, N, 5.29. Mass spectrum: parent ion at m/e 524.

Storage tests on these ruthenocenyl compounds for 6 months shows no apparent decomposition.

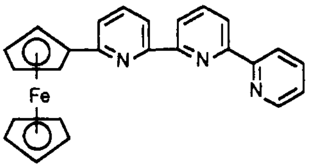
Preparation of the complexes $[(L)PdCl]$ (L = L1, L2) and $[(HL3)PdCl_2]$ was straightforward: (1,5-cyclooctadienyl)palladium dichloride and a 1.5 molar excess of the appropriate ligand (HL1 or HL2) were reacted overnight in dichloromethane. This contrasts with the reported preparations of (2,2′-bipyridyl)palladium dichloride complexes which require the addition of a small quantity of dilute hydrochloric acid to facilitate the reaction.[19] The derived purple complexes are all sparingly soluble in chloroform and dichloromethane: the crystalline complexes are considerably more difficult to dissolve than the powdered compounds. The analytical data were found to be unreliable since the compounds crystallized as solvates which had a tendency to lose solvent with time. Where possible, analytical data were based on the partial solvate nature of individual samples and an estimation of the quantity of solvent present in a particular sample was obtained from the integration of the ^{1}H NMR spectra. The palladium complexes have been stored in an aerobic environment for up to 2 years without apparent decomposition to the complex as a whole; however, further dichloromethane is lost with time.



HL1: M = Fe; R_1, R_2 = H
HL2: M = Fe; R_1 = H; R_2 = 2,2′-bipyrid-6-yl
HL5: M = Fe; R_1 = CH_2NMe_2; R_2 = H
HL6: M = Ru; R_1, R_2 = H
HL7: M = Ru; R_1 = H; R_2 = 2,2′-bipyrid-6-yl

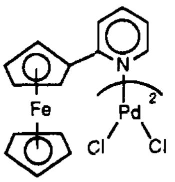


HL3: M = Fe; R = H
HL4: M = Fe; R = 1,10-phenanthrolin-2-yl
HL8: M = Ru; R = H



HL9

Examination of the ^{1}H NMR spectra of the derived complexes immediately indicated a difference between the complexes derived from the bipyridyl ligands and those derived from the 1,10-phenanthroline-based ligands. The bipyridyl complexes indicated the presence of a metalated ferrocene cyclopentadienyl ring, whereas the phenanthrolinyl complexes did not. Metalation of this type has been previously observed in the case of ferrocenylpyridine to give complex 2, shown previously. In the original work carried out on the metalation of pyridylferrocene with potassium tetrachloropalladate, it had been found that the bis(pyrid-2-ylferrocenyl)palladium dichloride complex 14 was formed immediately and could be isolated by precipitation from solution while the metalated species was formed in 20 h in the presence of sodium acetate. Under the reaction conditions employed here, the metalation reaction will be favored. It is possible that the excess ligand is partially responsible for absorption of the HCl generated in the complexation reaction. In some related recent work Constable and co-workers have observed the metalation of 6-phenyl-2,2′-bipyridine with potassium tetrachloropalladate in acetonitrile/water.[20] In the present case, the ferrocenyl ligand acts as a five-electron-donor system. The ^{1}H NMR spectrum of $[Pd(L2)Cl]\cdot 0.5CH_2Cl_2$ is shown in Figure 2f. There are seven independent ferrocenyl resonances, as expected by lowering of the symmetry on metalation. The proton resonances of the metalated cyclopentadienyl ring occur at δ 4.59, 4.46, and 4.86 for the protons α, β, and γ to palladium, respectively. The proton resonances of the unsubstituted ring show unusual marked chemical shift differences, especially for the cyclopentadienyl protons adjacent to the bipyridyl substituent (δ 4.91 and 5.48). This is indicative of a strong influence of the top substituted ring (see diagram) on the lower ring. In order to confirm these observations, the single-crystal X-ray structure determination of $[Pd(L2)Cl]\cdot 0.5CH_2Cl_2$ was undertaken. The speculations are borne out by the structural study (Figure 3), which shows that, in the solid state, the unmetalated bipyridyl substituent lies on the same side of the ferrocene as the metalated bipyridyl. The pyridyl ring containing N(3) is tilted very slightly so that N(3) is directed toward the palladium center; however, the actual interatomic distance between these atoms is long (~4.19 Å), which is almost equivalent to the intermolecular distance between Pd and N(1*) in the neighboring unit cell. Assuming free rotation of the pyridyl ring containing N(3), the closest possible interaction between Pd and N(3) would be approximately 2.3 Å, which compares relatively favorably with the observed bond lengths between palladium and N(1) and N(2) (2.00 and 2.16 Å, respectively). Such an interaction in the present circumstance is, of course, unfavorable since the integrity of the square-planar coordination would be lost. Of general interest, however, is why the bipyridyl substituents are found in the solid state on the same side when simple steric arguments would favor a 180° rotation of one



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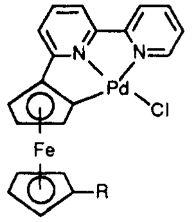
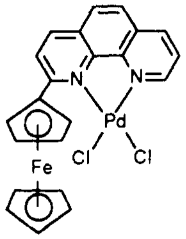


R = H ([Pd(L1)Cl]), 2,2′-bipyrid-6-yl ([Pd(L2)Cl])



$[Pd(HL3)Cl_2]$

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(19) Rotondo, E.; Tresoldi, G.; Faraone, F.; Pietropaolo, R. *Inorg. Chem.* **1976**, *15*, 2102.

(20) It is of interest to note here that Constable and co-workers[8c] observed that on reaction of 6-phenyl-2,2′-bipyridine with hydrated rhodium trichloride a single isomer of $[Rh(L)_2Cl_2]Cl$ was obtained. Similarly in the case of the ferrocene analogue HL1 a single isomer is obtained on its reaction with rhodium trichloride hydrate and ammonium hexafluorophosphate. The ^{1}H NMR spectrum of this complex shows two different ferrocenyl environments. The structure of the product from this reaction is currently being determined by X-ray crystallography.

Table II. Bond Distances (Å) and Angles (deg) for All Non-Hydrogen Atoms of $[Pd(2)Cl]\bullet 0.5CH_2Cl_2$

Pd–Cl	2.307 (5)	Pd–N(1)	1.998 (15)	C(3)–C(4)	1.40 (3)	C(4)–C(5)	1.42 (3)
Pd–N(2)	2.158 (16)	Pd–C(22)	1.926 (17)	C(5)–C(21)	1.47 (3)	C(6)–C(7)	1.42 (3)
Fe–C(21)	2.039 (18)	Fe–C(22)	2.092 (19)	C(7)–C(8)	1.30 (4)	C(8)–C(9)	1.39 (4)
Fe–C(23)	2.050 (20)	Fe–C(24)	2.02 (3)	C(9)–C(10)	1.39 (3)	C(11)–C(12)	1.39 (3)
Fe–C(25)	2.061 (22)	Fe–C(26)	2.029 (21)	C(11)–C(16)	1.50 (3)	C(12)–C(13)	1.35 (3)
Fe–C(27)	2.052 (24)	Fe–C(28)	2.036 (25)	C(13)–C(14)	1.33 (3)	C(14)–C(15)	1.42 (3)
Fe–C(29)	2.029 (19)	Fe–C(30)	2.045 (19)	C(15)–C(26)	1.51 (3)	C(16)–C(17)	1.37 (3)
Cl(2)–Cl(3)	2.820 (18)	Cl(2)–C(31)	1.72 (7)	C(17)–C(18)	1.38 (3)	C(18)–C(19)	1.36 (4)
Cl(3)–C(31)	1.63 (6)	N(1)–C(1)	1.356 (24)	C(19)–C(20)	1.35 (4)	C(21)–C(22)	1.45 (3)
N(1)–C(5)	1.32 (3)	N(2)–C(6)	1.35 (3)	C(21)–C(25)	1.42 (3)	C(22)–C(23)	1.42 (3)
N(2)–C(10)	1.33 (3)	N(3)–C(11)	1.39 (3)	C(23)–C(24)	1.41 (3)	C(24)–C(25)	1.41 (3)
N(3)–C(15)	1.316 (25)	N(4)–C(16)	1.31 (3)	C(26)–C(27)	1.40 (3)	C(26)–C(30)	1.41 (3)
N(4)–C(20)	1.30 (3)	C(1)–C(2)	1.39 (3)	C(27)–C(28)	1.34 (3)	C(28)–C(29)	1.40 (3)
C(1)–C(6)	1.44 (3)	C(2)–C(3)	1.38 (4)	C(29)–C(30)	1.44 (3)		
Cl(1)–Pd–N(1)	177.9 (5)	C(12)–C(11)–C(16)	123.6 (19)	C(11)–N(3)–C(15)	117.2 (15)	C(16)–N(4)–C(20)	120.8 (21)
Cl(1)–Pd–N(2)	100.7 (5)	Cl(1)–Pd–C(22)	98.4 (6)	N(1)–C(1)–C(2)	117.2 (19)	N(1)–C(1)–C(6)	114.9 (18)
N(1)–Pd–N(2)	79.1 (7)	N(1)–Pd–C(22)	81.8 (7)	C(2)–C(1)–C(6)	127.8 (19)	C(1)–C(2)–C(3)	120.0 (19)
N(2)–Pd–C(22)	160.9 (7)	C(21)–Fe–C(22)	41.0 (7)	C(2)–C(3)–C(4)	121.3 (19)	C(14)–C(15)–C(26)	121.6 (17)
C(21)–Fe–C(23)	66.4 (8)	C(21)–Fe–C(24)	67.2 (8)	N(4)–C(16)–C(11)	117.4 (18)	N(4)–C(16)–C(17)	121.0 (19)
C(21)–Fe–C(25)	40.6 (8)	C(21)–Fe–C(26)	111.8 (7)	C(11)–C(16)–C(17)	121.6 (20)	C(16)–C(17)–C(18)	118.9 (21)
C(21)–Fe–C(27)	124.7 (8)	C(21)–Fe–C(27)	124.7 (8)	C(17)–C(18)–C(19)	117.7 (21)	C(18)–C(19)–C(20)	120.4 (22)
C(12)–C(11)–C(16)	123.6 (19)	C(11)–C(12)–C(13)	121.1 (18)	N(4)–C(20)–C(19)	121.0 (23)	Fe–C(21)–C(5)	125.4 (14)
C(12)–C(13)–C(14)	118.8 (18)	C(13)–C(14)–C(15)	120.2 (18)	Fe–C(21)–C(22)	71.4 (11)	Fe–C(21)–C(25)	70.5 (11)
N(3)–C(15)–C(14)	122.4 (18)	N(3)–C(15)–C(26)	115.9 (16)	C(5)–C(21)–C(22)	114.1 (16)	C(5)–C(21)–C(25)	133.7 (17)
C(21)–Fe–C(28)	156.1 (9)	C(21)–Fe–C(29)	163.3 (9)	C(22)–C(21)–C(25)	112.2 (16)	Pd–C(22)–Fe	123.5 (9)
C(21)–Fe–C(30)	127.6 (8)	C(22)–Fe–C(23)	40.2 (7)	Pd–C(22)–C(21)	113.8 (12)	Pd–C(22)–C(23)	143.7 (16)
C(22)–Fe–C(25)	70.1 (7)	C(22)–Fe–C(24)	69.3 (7)	Fe–C(22)–C(21)	67.5 (10)	Fe–C(22)–C(23)	68.3 (11)
C(22)–Fe–C(26)	124.4 (7)	C(22)–Fe–C(27)	106.4 (8)	C(21)–C(22)–C(23)	102.4 (16)	Fe–C(23)–C(22)	71.5 (11)
C(22)–Fe–C(28)	118.4 (8)	C(22)–Fe–C(29)	153.5 (8)	Fe–C(23)–C(24)	68.5 (13)	C(22)–C(23)–C(24)	111.0 (17)
C(22)–Fe–C(30)	162.4 (8)	C(23)–Fe–C(24)	40.6 (9)	Fe–C(24)–C(23)	70.9 (13)	Fe–C(24)–C(25)	71.5 (14)
C(23)–Fe–C(25)	67.9 (8)	C(23)–Fe–C(26)	159.3 (9)	C(23)–C(24)–C(25)	109.1 (17)	Fe–C(25)–C(21)	68.2 (13)
C(23)–Fe–C(27)	122.4 (9)			C(21)–C(25)–C(24)	105.1 (17)	Fe–C(26)–C(27)	70.9 (13)
C(23)–Fe–C(28)	106.2 (8)	C(23)–Fe–C(29)	120.0 (8)	Fe–C(26)–C(30)	70.3 (12)	C(15)–C(26)–C(30)	125.5 (17)
C(23)–Fe–C(30)	157.1 (9)	C(24)–Fe–C(25)	40.3 (9)	C(15)–C(26)–C(27)	126.0 (18)	C(27)–C(26)–C(30)	108.5 (17)
C(24)–Fe–C(26)	159.7 (8)	C(24)–Fe–C(27)	157.7 (9)	Fe–C(27)–C(26)	69.1 (13)	Fe–C(27)–C(28)	70.2 (15)
C(24)–Fe–C(28)	123.0 (9)	C(24)–Fe–C(29)	106.8 (9)	C(26)–C(27)–C(28)	108.9 (19)	C(3)–C(4)–C(5)	116.5 (20)
C(24)–Fe–C(30)	122.6 (9)	C(25)–Fe–C(26)	125.4 (8)	N(1)–C(5)–C(4)	119.9 (18)	N(1)–C(5)–C(21)	112.7 (17)
C(25)–Fe–C(27)	160.6 (8)	C(25)–Fe–C(28)	160.2 (9)	C(4)–C(5)–C(21)	127.4 (19)	N(2)–C(6)–C(1)	117.9 (18)
C(25)–Fe–C(29)	124.8 (9)	C(25)–Fe–C(30)	109.6 (8)	N(2)–C(6)–C(7)	117.9 (21)	C(1)–C(6)–C(7)	124.1 (21)
C(26)–Fe–C(27)	40.0 (8)	C(26)–Fe–C(28)	66.6 (8)	C(6)–C(7)–C(8)	119.4 (23)	C(7)–C(8)–C(9)	122.0 (22)
C(26)–Fe–C(29)	68.0 (8)	C(26)–Fe–C(30)	40.6 (8)	C(8)–C(9)–C(10)	118.8 (23)	N(2)–C(10)–C(9)	118.6 (22)
C(27)–Fe–C(28)	38.4 (9)	C(27)–Fe–C(29)	66.8 (9)	N(3)–C(11)–C(12)	120.2 (18)	N(3)–C(11)–C(16)	116.2 (17)
C(27)–Fe–C(30)	67.7 (9)	C(28)–Fe–C(29)	40.3 (10)	Fe–C(28)–C(27)	71.5 (14)	Fe–C(28)–C(29)	69.6 (13)
C(28)–Fe–C(30)	68.0 (8)	C(29)–Fe–C(30)	41.3 (8)	C(27)–C(28)–C(29)	109.7 (18)	Fe–C(29)–C(28)	70.1 (13)
Cl(3)–Cl(2)–C(31)	31.8 (18)	Cl(2)–Cl(3)–C(31)	33.6 (19)	Fe–C(29)–C(30)	70.7 (10)	C(28)–C(29)–C(30)	107.2 (19)
Pd–N(1)–C(1)	117.4 (14)	Pd–N(1)–C(5)	117.5 (12)	Fe–C(30)–C(26)	69.1 (11)	Fe–C(30)–C(29)	68.8 (11)
C(1)–N(1)–C(5)	125.0 (17)	Pd–N(2)–C(6)	110.5 (14)	C(26)–C(30)–C(29)	105.6 (18)	Cl(2)–C(31)–Cl(3)	114 (3)
Pd–N(2)–C(10)	126.2 (14)	C(6)–N(2)–C(10)	123.2 (17)				

of the cyclopentadienyl rings. It is possible that intermolecular attractions are responsible, in this particular crystal lattice geometry, together with the weak influence of N(3) on palladium. In the insert in Figure 3, it can be seen that the ferrocenyl rings are almost totally eclipsed. The dihedral angles between the pyridyl rings as shown in Figure 3 are 2.1 (8)° for AB, 9.1 (8)° for CD, and 175.5 (7)° for AC. The dihedral angle for the cyclopentadienyl rings is 176.9 (10)°. The possibility presumably exists to coordinate a second metal to the pendant bipyridyl substituents. Efforts in this direction are underway.

The reaction of the ferrocenylterpyridyl derivative HL9 with (1,5-cyclooctadienyl)palladium dichloride results in a mixture of compounds from which the soluble (in CH_2Cl_2) deep purple microcrystalline complex can be obtained in low yield (Scheme I). A black residue is also obtained which is presumably oligomeric or polymeric material caused by coordination of the palladium to more than one ligand. The possibility also exists again for metalation of the ferrocenyl ring and coordination of up to three nitrogen atoms, in which case a cationic complex might be expected with presumably lower solubility in weakly polar organic solvents.

The new ligand HL5 was prepared from the direct reaction of 2-lithio-1-((dimethylamino)methyl)ferrocene[11] with 2,2′-bipyridine, using a procedure identical that previously used in the synthesis of HL1.[6] The synthesis of HL5 can be taken as a prototype reaction for the synthesis of chiral ligands, since adaptation to using chiral 1-((dimethylamino)ethyl)ferrocene, which is available commercially and is simple to synthesize,[21] would result in chiral ligands. Compound HL5 was initially isolated as a yellow oil which, following chromatography, gave red-black nodules on subsequent crystallization. The bipyridyl proton resonances of HL5 on average are shifted upfield by 0.16 ppm in comparison to bipyridine, the result of increased basicity of the cyclopentadienyl ring caused by stronger σ-donation to the dipyridyl ring. The reaction of HL5 with (1,5-COD)$PdCl_2$, under conditions identical to those previously described, gave an inseparable mixture of products. ^1H NMR spectra of the powder obtained indicated the presence of three complexes in differing proportions. Attempted crystallization of the powder gave only microcrystalline material. In one of these complexes,

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(21) (a) Hauser, C. R.; Lindsay, J. K. *J. Org. Chem.* **1957**, *22*, 906. (b) Gokel, G. W.; Ugi, I. K. *J. Chem. Educ.* **1972**, *49*, 292. (c) Herrman, R.; Ugi, I. K. *Tetrahedron* **1981**, *37*, 1001. (d) Herrman, R.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 956. (e) Butler, I. R.; Cullen, W. R. *Can. J. Chem.* **1983**, *61*, 2354. (f) Sihler, R.; Werz, U.; Brune, H.-A. *J. Organomet. Chem.* **1989**, *368*, 213.

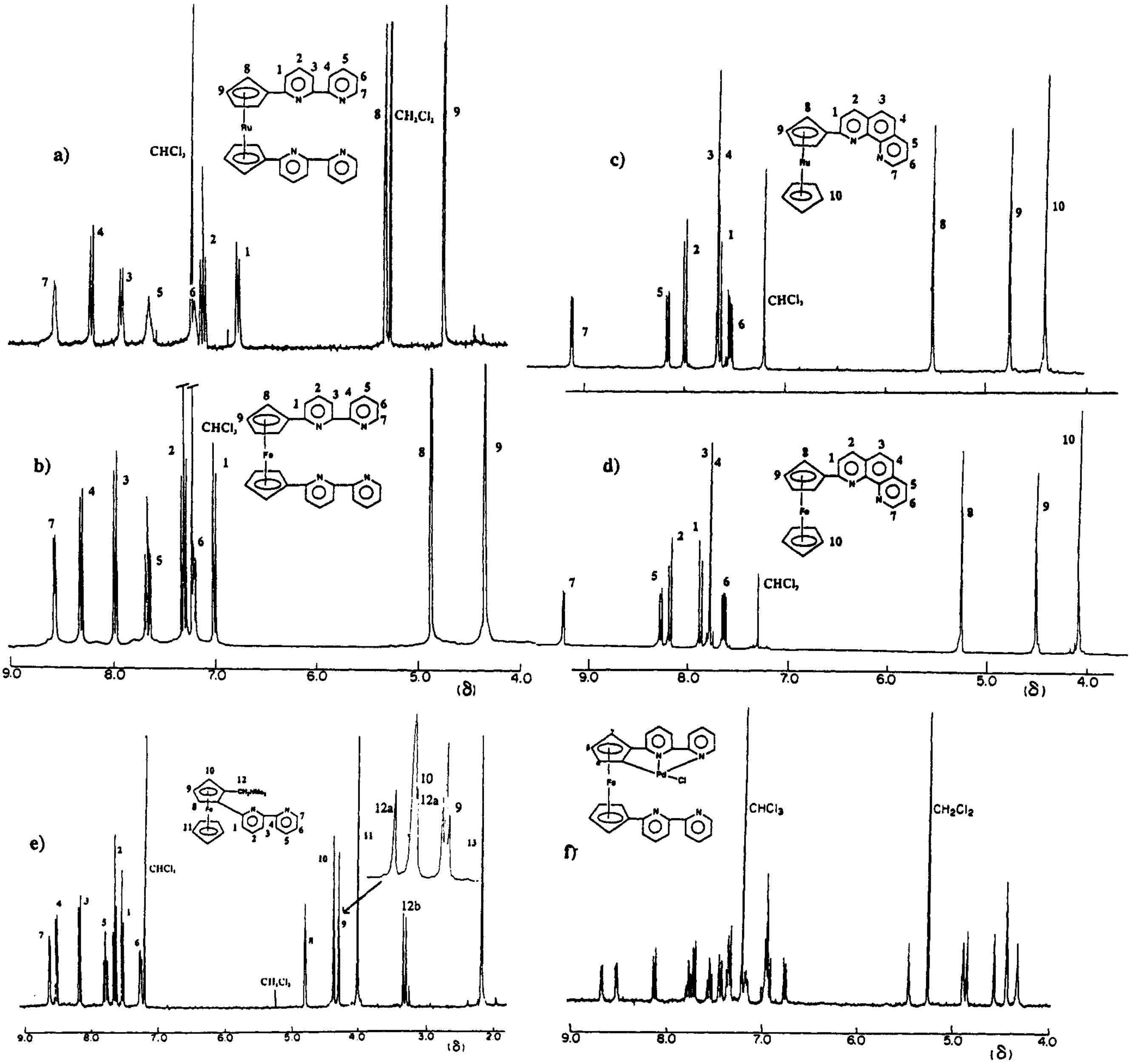
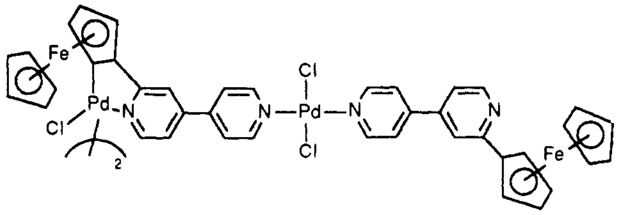


Figure 2. ^{1}H NMR spectral comparison of chemical shifts of (a) bis-2,2′-bipyrid-6-yl)ruthenocene (HL7), (b) bis(2,2′-bipyrid-6-yl)ferrocene (HL2), (c) 2-ruthenocenyl-1,10-phenanthroline (HL8), (d) 2-ferrocenyl-1,10-phenanthroline (HL3), (e) 2-(2,2′-bipyridyl)-1-((dimethylamino)methyl)ferrocene (HL5), and (f) [Pd(2)Cl]·0.5CH$_2$Cl$_2$. N.B.: A simplified proton numbering scheme has been adopted.

a very low field resonance at 9.37 ppm is observed. This compares with those of the other two complexes in the mixture, with lowest field resonances at 8.85 and 8.65 ppm, respectively. In comparison to the resonances observed in [(L)PdCl] (L = L1, L2), the last two complexes can be assigned to cyclometalated species. In addition, in two of the complexes, the dimethyl-substituted nitrogen is bound to palladium, as witnessed by the appearance of the characteristic individual resonances of the *N*-methyl groups. Attempted recrystallization from DMSO, in which the mixture is soluble, was unsuccessful. It should also be noted here that if the metalation reaction occurs, the HCl produced could react to quaternize the pendant amine, to give a less soluble salt. The reaction of 2-ferrocenyl-4,4′-bipyridine with (1,5-COD)PdCl$_2$ resulted in the formation of a red-brown polymeric material which was insoluble in methanol and dichloromethane. Mass spectroscopy of this material indicated the presence of a strong peak at the unassignable *m*/*e* values 529, 451, 393, and 373, in addition to that of the ligand at *m*/*e* 340. The material is probably a mixture resulting from partial coordination to more than one nitrogen atom:



possible palladium coordination in (4,4′-bipyridyl)ferrocene complex

This result is comparable to those of Unson and coworkers, who found similar results on attempted complexation of 4,4′-bipyridine with palladium.[22]

A small-scale reaction of 6-ruthenocenyl-2,2′-bipyridine with an excess of (η^4-1,5-cyclooctadienyl)palladium di-

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(22) Unson, R.; Fornies, J.; Naaro, R.; Gallo, A. *Transition Met. Chem.* **1980**, *5*, 284.

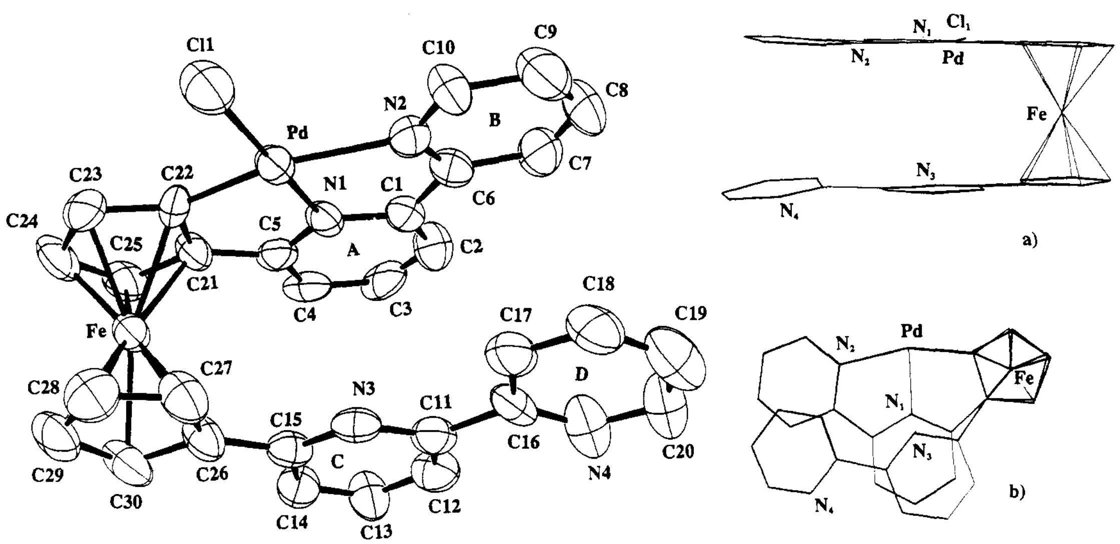
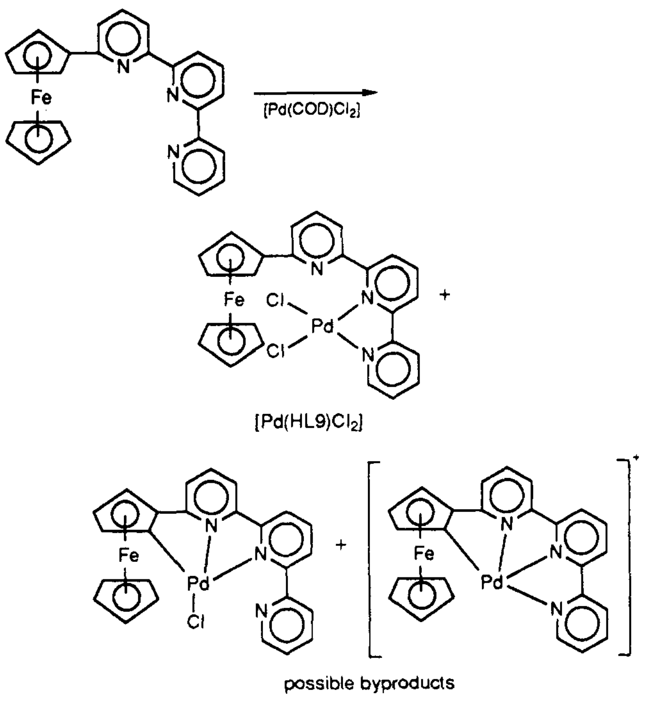
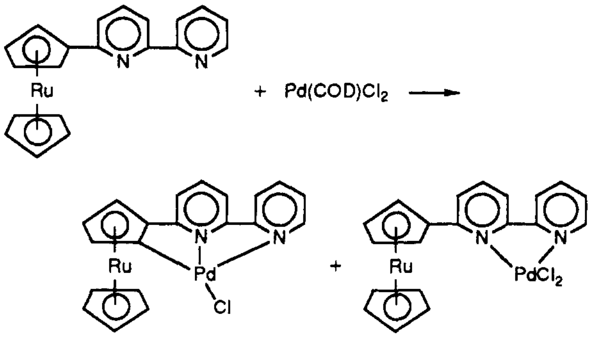


Figure 3. Single-crystal X-ray structure of [Pd(L2)Cl]·$0.5CH_2Cl_2$, showing the numbering scheme (the solvent molecule has been omitted). Inserts show stick diagrams to highlight (a) the coplanar nature of pyridyl rings with respect to the ferrocenyl cyclopentadienyl rings and (b) the eclipsed nature of the cyclopentadienyl ring.

Scheme I



chloride in dichloromethane gave a mixture of the red metalated and orange unmetalated complexes, which were identified by their characteristic ^1H NMR spectra in the cyclopentadienyl proton region (δ 4.4–5.85).



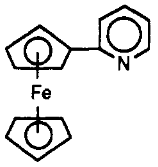
(1)

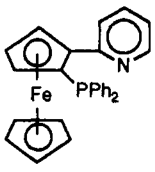
In the case of both metalated complexes, ^1H NMR spectroscopy offers a strong indication that the ligand acts as a good electronic reservoir, with upfield shifts observed for some of the heterocyclic base proton resonances, whereas in the case of the dichloride complex all observed shifts are downfield. This implies that the effect of the chlorides is significant in removing electron density from the palladium center. On removal of one chloride, there is a marked upfield shift of all resonances, indicating reduced σ-donation of the bipyridyl ligands to the palladium center.

On coordination with palladium dichloride, both the 2-ferrocenyl and 2-ruthenocenyl-1,10-phenanthroline compounds cleanly gave the N,N′-derivatives, which were deep violet and orange, respectively. In each case, relatively large downfield ligand resonance shifts are observed on coordination, the largest being that of H-9 adjacent to the coordinated nitrogen atom (δ 0.29 and 0.34, respectively, for the ferrocenyl and ruthenocenyl ligands). The larger shifts of H-7 and H-9 (δ ~0.3) in comparison to that of H-8 (δ ~0.17) is due to resonance stabilization. The smallest shift of a phenanthrolinyl proton resonance on coordination is for proton H-4 in each case. This is at a remote site to the palladium. The α-cyclopentadienyl resonances are shifted downfield by approximately 0.23 ppm, indicated the transfer of electron density to the phenanthrolinyl moiety, allowing stronger σ-donation of the nitrogen to palladium. Interestingly, the unsubstituted cyclopentadienyl ring, in the case of the ruthenocenyl ligand, is shifted downfield (δ 0.28), while no such shift is observed in the case of the ferrocene-based ligand.

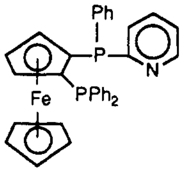
The potential structural modification of ferrocenyl- and ruthenocenylbipyridine ligands is of interest; thus, we decided to explore the possibility of stereoselective lithiation of the ferrocenyl rings. In preparation, we carried out test reactions with 2-pyridylferrocene, which is known to lithiate stereoselectively.

For example, the treatment of 2-pyridylferrocene with n-butyllithium in diethyl ether, followed by reaction of chlorodiphenylphosphine, gave PPh_2L10 in reasonable (35% isolated) yield. Similarly, ring cleavage of ferrocenediylphenylphosphine[13] by 2-lithiopyridine, generated in situ, gave compound L11. In a small-scale test reaction, treatment of ferrocenediylphenylphosphine with phenyllithium and then pyridine gave HL12, although in rather low yields. Compounds PPh_2L10, L11, and HL12 are readily identifiable by their characteristic ^1H NMR spectra. For example, the spectrum of PPh_2L10 shows three reso-

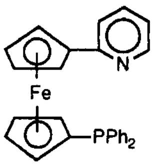




PPh$_2$L10



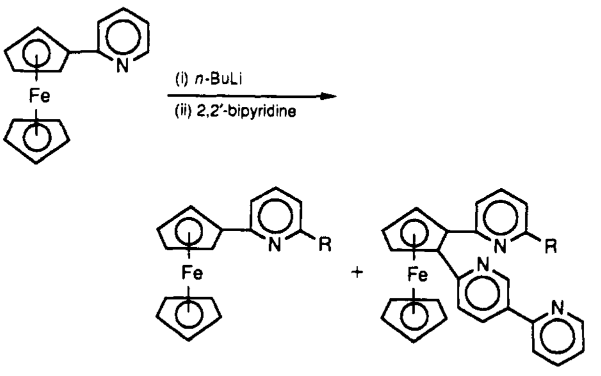
L11



HL12

nances in the cyclopentadienyl region for the substituted ring, one of which lies upfield at δ 3.73 from the singlet resonance of the unsubstituted ring (δ 4.03). The upfield proton is assigned to the proton adjacent to the phosphorus atom since a characteristic ^{31}P–H coupling is observed. The remaining two protons resonate at δ 4.43 (β to P) and 5.10 (α to pyridyl substituent). The latter resonance occurs at fairly low field when compared with that of, for example, 2-pyridylferrocene, (4-*tert*-butylpyridyl)ferrocene, and (4-phenylpyridyl)ferrocene, which have chemical shifts of δ 4.90, 4.89, and 4.97, respectively, for the analogous protons. In the case of compound L11, all four protons on the substituted ring are nonequivalent magnetically, due to the asymmetric substituent. The resonances occur at δ 4.04, 4.35, 4.38, and 4.44, respectively. Compound HL12 exhibits four ferrocenyl multiplet resonances as anticipated.

A reaction of 2-pyridylferrocene with *n*-butyllithium for 24 h, followed by subsequent treatment with 2,2′-bipyridyl, gave only a mixture of products. The major products, identified by a TLC comparison with authentic samples, were the (2-butylpyridyl)ferrocene and the starting compound. Only small quantities of bipyridyl-containing products could be observed, which were not considered worth isolating since it seemed from TLC that a large number (seven) of products were present with similar R_f values. However, it was found that lithiation for 40–50 min followed by reaction with 2,2′-bipyridyl was more successful with higher product yields of 1-(2-pyridyl)-2-(2,2′-bipyrid-6-yl)ferrocene (L13; eq 2) being obtained; however, attempts at chromatographic separation of the a pure sample failed due to decomposition on the support and the presence of trace impurities. We are currently attempting the separations using a chromatatron, and results in this area will be published at a later date. In some elegant pioneering work, Booth and Rockett had investigated the lithiation of 2-pyridylferrocene with *n*-BuLi.[12] The results obtained have substantiated their results, in that only very short lithiation periods are required to obtain optimum product yields.



(2)

R = H (L13), *n*-butyl

The reaction of 6-ferrocenyl-2,2′-bipyridine with excess *n*-butyllithium was carried out for different time periods to test the possibility of producing a directed lithiation of the ferrocenyl rings. Following reaction for 20 h, the mixture was quenched with D$_2$O and the product solution characterized by ^{1}H NMR and mass spectroscopy. Although the ferrocenyl rings had been stereoselectively lithiated at the α-position of the substituted ring, as witnessed by deuterium incorporation at this position ($\sim$57%), it was equally evident that nucleophilic substitution of the distal pyridyl ring had occurred at the 6′-position to give a large quantity of the 6-ferrocenyl-6′-*n*-butyl-2,2′-bipyridine (parent ion m/e 397 for the monodeuterio compound). In addition, some dibutylated derivative of 6-ferrocenyl-2,2′-bipyridine was observed, although the position of the second butyl group is unclear due to resonance overlap in the ^{1}H NMR spectrum. We conclude from these results that the direct lithiation for prolonged time periods is not useful for the synthesis of substituted derivatives, unlike the reaction of pyridylferrocene. However, on reaction with *n*-butyllithium for 40 min, followed by quenching with chlorodiphenylphosphine, we find that the reaction is synthetically feasible, and this will be the subject of a later series of publications.[23]

Acknowledgment. The work described was funded partially in the form of an operating grant from the Natural Sciences and Engineering Research Council of Canada to I.R.B. Palladium in the form of the dichloride was supplied on loan from Johnson-Mathey Ltd., to whom we are grateful. The structural determination was carried out at the National Research Council of Canada by I.R.B. with the guidance of Drs. Eric Gabe and Yvon Le Page. I.R.B. thanks Dr. E. C. Constable of Cambridge University for the use of preliminary reports of his work prior to publication.

Registry No. **HL1**, 131192-54-6; Pd[**L1**]Cl, 137396-37-3; **HL2**, 137396-27-1; Pd[**L2**]Cl, 137396-38-4; Pd[**L2**]Cl·0.5CH$_2$Cl$_2$, 137396-48-6; **HL3**, 131192-55-7; Pd[**HL3**]Cl$_2$, 137396-39-5; **HL4**, 131207-17-5; **HL5**, 137396-28-2; Pd[**L5**]Cl, 137396-40-8; Pd[**HL5**]Cl$_2$, 137396-41-9; **HL6**, 137396-29-3; Pd[**L6**]Cl, 137396-42-0; Pd[**HL6**]Cl$_2$, 137396-43-1; **HL7**, 137396-30-6; **HL8**, 137396-31-7; Pd[**HL8**]Cl$_2$, 137396-44-2; **HL9**, 137396-32-8; Pd[**HL9**]Cl$_2$, 137396-45-3; **PPh$_2$L10**, 137396-33-9; Pd[**PPh$_2$L10**]Cl$_2$, 137396-46-4; **L11**, 137396-34-0; **HL12**, 127688-63-5; **L13**, 137396-35-1; **14**, 137396-36-2; (1,5-COD)PdCl$_2$, 12107-56-1; C$_{28}$H$_{30}$D$_2$FeN$_2$, 137396-60-2; C$_{24}$H$_{23}$DFeN$_2$, 137396-47-5; 1-((dimethylamino)methyl)ferrocene, 1271-86-9; 2-pyridylferrocene, 12216-00-1; 1,1′-ferrocenediylphenylphosphine, 72954-06-4; (*n*-butylphenylphosphino)ferrocene, 131192-30-8; (2-pyridyl)phenylferrocenylphosphine oxide, 137396-49-7; 2,2′-bipyridine, 366-18-7.

Supplementary Material Available: Listings of positional parameters, all bond distances and angles, thermal parameters, and torsion angles for (L2)PdCl·0.5CH$_2$Cl$_2$ (10 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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[23] A convenient method to circumvent the problems associated with *n*-butyl substitution of the pyridyl rings is to prepare the metalated organomercurial (L)HgCl and subsequently treat this with *n*-butyllithium.