12, 32609-75-9; 13, 106682-38-6; 14, 81753-16-4; 15, 81753-17-5; 16, 106682-39-7; 17, 112022-78-3; 18, 112022-80-7; (η^5-C_5Me_5)(PMe_3)Rh(*m*-$C_6H_4CH_3$)(H), 81971-47-3; (η^5-C_5Me_5)(PMe_3)Rh(*p*-$C_6H_4CH_3$)(H), 81971-48-4; (η^5-C_5Me_5)(PMe_3)Rh(C_6H_5)(H), 81971-46-2; *p*-ClC_6H_4CN, 623-03-0.

Supplementary Material Available: Listings of all positional and thermal parameters and interatomic distances and angles for **7a** and **16** (9 pages); listings of structure factors for **7a** and **16** (24 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of New (η^6-Substituted indole)(η^5-cyclopentadienyl)ruthenium Complexes. Nucleophilic Displacement upon (η^6-4- or η^6-5-Chloroindole)(η^5-cyclopentadienyl)ruthenium(II) Hexafluorophosphates

Robert M. Moriarty,* Yi-Yin Ku, and U. S. Gill

Department of Chemistry, University of Illinois at Chicago, P.O. Box 4348, Chicago, Illinois 60607

Received June 29, 1987

(η^5-Cyclopentadienyl)tris(acetonitrile)ruthenium(II) hexafluorophosphate undergoes smooth thermal ligand exchange reaction with a variety of indole substrates to yield new complexes in which all three acetonitrile molecules have been replaced. Complexes prepared by this method are [(η^6-indole)RuCp]PF_6, [(η^6-*N*-methylindole)RuCp]PF_6, [(η^6-5-methyl-*N*-methylindole)RuCp]PF_6, [(η^6-5-bromoindole)RuCp]PF_6, [(η^6-5-chloro-*N*-methylindole)RuCp]PF_6, [(η^6-4-chloro-*N*-methylindole)RuCp]PF_6, and [(η^6-5-chloroindole)RuCp]PF_6. Complexes [(η^6-5-chloro-*N*-methylindole)RuCp]PF_6 and [(η^6-4-chloro-*N*-methylindole)RuCp]PF_6 undergo substitution of the chlorine atom with anions generated (NaH/THF) from dimethyl malonate, diethyl malonate, mercaptoacetic acid, and benzyl alcohol. Complexes prepared in this study were [(η^6-5-(dicarbomethoxymethyl)-*N*-methylindole)RuCp]PF_6, [(η^6-4-(dicarbomethoxymethyl)-*N*-methylindole)RuCp]PF_6, [(η^6-5-(dicarbethoxymethyl)-*N*-methylindole)RuCp]PF_6, [(η^6-4-(dicarbethoxymethyl)-*N*-methylindole)RuCp]PF_6, [(η^6-5-((*S*)-(carboxymethyl)thio)-*N*-methylindole)RuCp]PF_6, [(η^6-4-((*S*)-(carboxymethyl)thio)-*N*-methylindole)RuCp]PF_6, and [(η^6-5-(phenylmethoxy)-*N*-methylindole)RuCp]PF_6. Similarly, nucleophilic substitution reaction of [(η^6-5-chloro-*N*-methylindole)RuCp]PF_6 with methanol in the presence of excess KOH (20 molar equiv) gave [(η^6-5-methoxy-*N*-methylindole)-RuCp]PF_6. Complex [(η^6-5-(methylamino)-*N*-methylindole)RuCp]PF_6 was obtained from reaction of [(η^6-5-chloro-*N*-methylindole)RuCp]PF_6 with methylamine (40% aqueous solution). Synthesis of complex [(η^6-5-(dicarbomethoxymethyl)indole)RuCp]PF_6 from complex [(η^6-5-chloroindole)RuCp]PF_6 is described using the *tert*-butyldimethylsilyl N-protecting group. Structural data such as IR, ^1H NMR, ^{13}C NMR, and microanalysis are given.

Indoles substituted at the C_4, C_5, C_6, and C_7 positions make up an important class of compounds that includes ergot alkaloids,[1] calabar bean alkaloids,[2] marine indoles,[3] synthetic β-blockers,[4] and psilocin analogues.[5] These compounds have many uses. For example, they act as adrenergics,[6] cholinergics,[7] antibiotics,[8] tumor promoters,[9] and fungicides.[10] Methods for synthesizing the 4-, 5-, 6-, or 7-substituted indole systems have so far fallen into three categories.[11] The first category includes the Leimgruber–Batcho method that proceeds from an appropriately substituted *o*-nitrotoluene and then construction of the fused pyrrole.[12] Another method in this category combines the Fischer indole reaction with the Japp–Klingemann reaction. In this method, the substituents are placed at the desired position on the indole by preselection in the benzene ring.[13] Methods in the second category start with an intact pyrrole ring and build up the benzene ring. For example, the benzene ring can be built up by photooxygenation of the pyrrole,[14] by employing the Diels–Alder

(1) For an excellent review see: Floss, H. G. *Tetrahedron* **1976**, *32*, 873. Berde, B., Schild, H. O., Eds. *Ergot Alkaloids and Related Compounds*; Springer-Verlag: New York, 1978.
(2) Robinson, B. In *The Alkaloids*; Manske, R. H. F., Holmes, H. L., Eds.; Academic: New York, 1967; Vol. X, Chapter 5.
(3) Christophersen, C. *Marine Indoles in Marine Natural Products*: Chemical and Biological Perspectives: Scheuer, P. J., Ed.; Academic: New York, 1982; Vol. V, pp 259–285. Liang, H.-T.; Hsu, H.-D.; Chang, C. P.; Ku, H.-E. *Chem. Abstr.* **1976**, *34*, 129.
(4) E.g. pindolol: Tsuda, Y.; Yoshimoto, K.; Nislikawa, T. *Chem. Pharm. Bull.* **1981**, *29*, 3593.
(5) Repke, D. B.; Ferguson, W. J. *J. Heterocycl. Chem.* **1982**, *19*, 845.
(6) E.g. 5,7-Dihydroxytryptamine as a substrate for indolamine neurons: Baumgarten, H. G.; Lachenmayer, L.; Zellforsch, Z. **1972**, *135*, 399.
(7) Gearien, J. E. *Cholinergics and Anticholinesterases in Medicinal Chemistry*; Burger, A., Ed., Wiley-Interscience: New York, 1970; pp 1307–1310.
(8) E.g. 4,6-Dihydroxy or 6,7-dihydroxyindoles from marine sources: see ref. 3.
(9) E.g. Teleocidin B: Takashima, M.; Sakai, H. *Ag. Biol. Chem.* **1960**, *24*, 647.
(10) Polyhalogenated indoles possess strong antifungal activity.[3]
(11) For a review see: Kozikowski, A. P. *Heterocycles* **1981**, *16*, 267.
(12) Leimgruber, W.; Batcho, A. D. *Abstracts of Papers*, Third International Congress of Heterocyclic Chemistry, Sandai, Japan, Aug 1971; U.S. Patent 3976639, 1976. Clark, R. D.; Repke, D. B. *Heterocycles* **1984**, *22*, 195.
(13) Nagasaka, T.; Yuge, T.; Ohki, S. *Heterocycles* **1977**, *8*, 371.
(14) Natsume, M.; Muratke, H. *Tetrahedron Lett.* **1979**, 3477.

0276-7333/88/2307-0660$01.50/0

reaction,[15] 1,3-dipolar cycloaddition,[16a] or more elaborate syntheses.[16] Methods in the third category begin with an intact indole ring but employ either intramolecular electrophilic,[17] radical reaction,[18a] or ipso substitution.[18b]

What is missing from this area of synthesis is direct nucleophilic displacement of a ring halogen by a carbanion or other desirable potential substituent. Recently we demonstrated that complexing aryl chlorides with $(CpFe^+)PF_6^-$ activated the ring halogen toward nucleophilic displacement.[19a-c] Unfortunately, the reaction conditions ($AlCl_3$, Al, high temperature) necessary for ligation of the $Cp(Fe^+)PF_6^-$ ligand are not compatible with the survival of the indole ring system. In order to activate the ring halogen by attachment of a metal ligand, we turned to ruthenium coordination chemistry and now report the synthesis of various [(η^5-Cp)Ru(η^6-indole substrates)]PF_6 complexes and nucleophilic displacement reactions of novel [(η^5-Cp)Ru(η^6-4- or η^6-5-chloroindole)]PF_6.

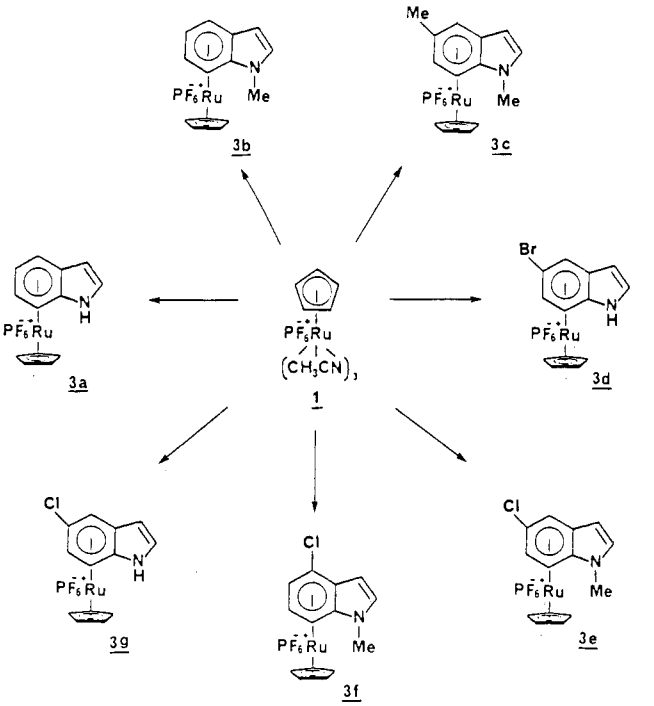
The 4- or 5-chloroindole undergoes ligand exchange with *tris*(acetonitrile)(cyclopentadienyl)ruthenium hexafluorophosphate (1) to yield the desired complexes. The choice of 4- or 5-chloroindole is dictated by the fact that substitution at the 4- and 5-positions leads to intermediates on the way to several naturally occurring indole alkaloids.

Results and Discussion

Synthesis and Characterization of New (η^6-Substituted indole)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphates. Salts of the dications (η^6-indole)(η^5-C_5Me_5)M^{2+} (M = Rh, Ir, or Co) were prepared by White and co-workers,[20,21] but their relative instability has precluded their use in organic synthesis. Moreover, Friedel–Crafts catalyzed Cp/arene exchange in ferrocene[22a,b] or ruthenocene[23a-c] is not possible with indole as a route to the corresponding (η^6-indole)(η^5-Cp)M^+ (M = Fe or Ru) complexes. The ready availability of [$CpRu(CH_3CN)_3$]PF_6 (1)[24a] and the thermal lability of acetonitrile ligands[24a,25] prompted us to attempt the synthesis of (η^6-indole)(η^5-Cp)Ru^{II} complexes from complex 1 and an appropriate indole substrate (Scheme I).

The new indole complexes **3a–g** were prepared by heating (40–45 °C) 1,2-dichloroethane solutions of the appropriate indole substrate **2a–g** (1.5 mmol) with

Scheme I



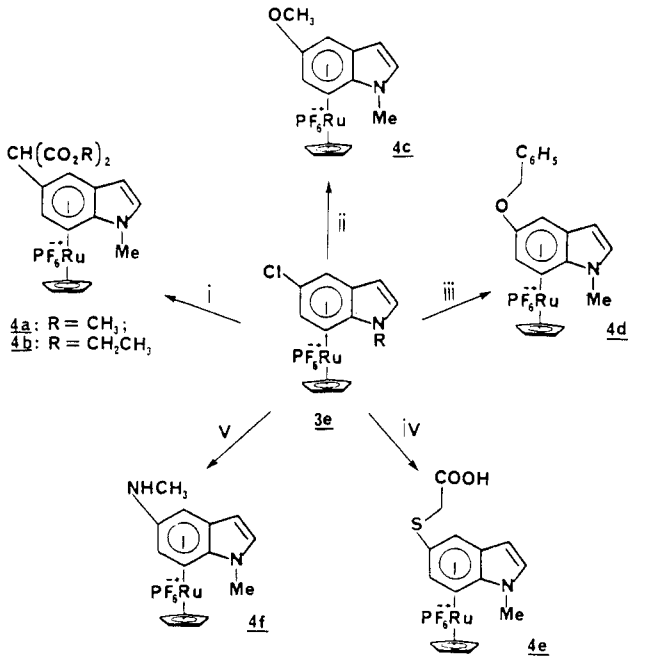
40 - 50° C, 15 h, 1,2-Dichloroethane, Indole Substrate.

[$CpRu(CH_3CN)_3$]PF_6 (1) for 15 h under N_2. The solvent was removed in vacuo, the residue was washed with ether, and the solid was collected and crystallized (CH_2Cl_2/ether) to produce yellow complexes **3a–g** in very high yields. These new complexes are thermally stable, crystalline solids, unlike the corresponding polyaromatic ligand complexes (e.g. phenanthrene, naphthalene, and anthracene).[25] It is interesting to note that these complexes showed very little decomposition with no apparent exchange reaction when refluxed in CH_3CN for 24 h. A notable feature of the present method is the ease with which one can attach the (η^5-cyclopentadienyl)ruthenium ($CpRu^+$) unit to η^6-aryl ring of the indole substrates.

The structure for complexes **3a–g** was assigned on the basis of elemental analyses as well as high-resolution ^1H and ^{13}C NMR (400-MHz) spectral analysis. It should be noted that NMR spectral data on metal complexes of η^6-indoles are rather rare, being limited to the tricarbonylchromium complexes of η^6-indole and η^6-*N*-methylindole[26] and the $(C_5Me_5)Rh^{III}$, $(C_5Me_5)Ir^{III}$, and $(C_5Me_5)Co^{III}$ complexes of η^6-indole.[20,21] Comparison of NMR spectral data for the η^6-indole complexes of other metals, e.g. rhodium,[20] iridium,[20] cobalt,[21] and chromium,[26] to ruthenium is instructive. The ^1H NMR resonances for the ring protons of complexes **3a–g** are shifted upfield in the range usually of –0.4 to –0.6 ppm compared to the free ligand. This shift is very similar to the upfield shifts of aromatic protons of cyclopentadienylruthenium complexation of simple arenes.[23b,c] However, the olefinic protons of the pyrrole ring of complexes **3a–g** show a downfield shift of +0.2 to +0.6 ppm relative to the free ligand. Typically, the ^1H NMR resonances for the aryl ring protons of complex **3b** appear in the range δ 7.0–5.9. This phenomenon represents significant shielding of these protons compared to the chemical shifts δ 7.9–7.1 of the corresponding protons in dicationic metal complexes[20,21]

(15) Kozikowski, A. P.; Kuniak, M. P. *J. Org. Chem.* **1978**, *43*, 2083.
(16) (a) Kozikowski, A. P. and Cheng, X.-M. *Tetrahedron Lett.* **1985**, 4047. (b) Trost, B. M.; Reiffen, M.; Crimmen, M. *J. Am. Chem. Soc.* **1979**, *101*, 257. (c) Muratake, H. and Mitsutaka, N. *Tetrahedron Lett.* **1987**, 2265.
(17) Kornfeld, E. K.; Fornefeld, E. J.; Kline, G. B.; Mann, M. J.; Morrison, D. E.; Jones, R. G.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *78*, 3087.
(18) (a) Anderson, N. G.; Lawton, R. G. *Tetrahedron Lett.* **1977**, 1843. (b) Barrett, A. G. M.; Dauzonne, D.; O'Neil, I. A.; Renaud, A. *J. Org. Chem.* **1984**, *49*, 4409.
(19) (a) Moriarty, R. M.; Gill, U. S. *Organometallics* **1985**, *5*, 253. (b) Gill, U. S.; Moriarty, R. M. *Synth. React. Inorg. Met.-Org. Chem.* **1986**, *16*, 485. (c) Gill, U. S.; Moriarty, R. M. *Synth. React. Inorg. Met.-Org. Chem.* **1986**, *16*, 1103.
(20) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654.
(21) White, C.; Fairhurst, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1531.
(22) (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Tetrahedron Lett.* **1963**, 1725. (b) For a review see: Sutherland, R. G. *J. Organomet. Chem., Libr.* **1977**, *3*, 311.
(23) (a) Roman, E.; Astruc, D. *Inorg. Chim. Acta* **1979**, *37*, L465. (b) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N.; Shulpina, L. S. *J. Organomet. Chem.* **1979**, *182*, C36. (c) Vol'kenau, N. A.; Bolesova, I. N.; Shul'pina, L. S.; Kitaigorodskii, A. N.; Kravtsov, D. N. *J. Organomet. Chem.* **1985**, *288*, 341.
(24) (a) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485. (b) Zelonka, R. A.; Baird, M. C. *J. Organomet. Chem.* **1972**, *44*, 383.
(25) McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519.
(26) Boutonnet, J. C.; Levisalles, J.; Rose, E.; Precigoux, G.; Courseille, C. *J. Organomet. Chem.* **1983**, *255*, 317.

Scheme II



(i) $H_2C(CO_2R)_2$ (2 eq), NaH (2 eq), THF, 40-50°, 10 h; H_3O^+, NH_4PF_6

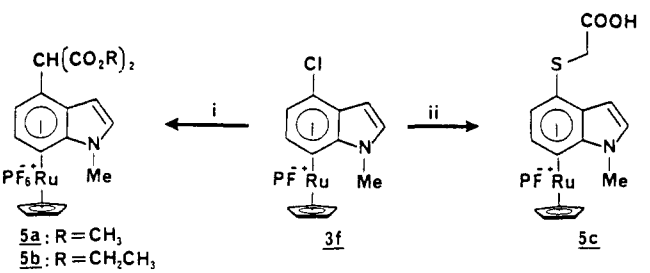
(ii) NaOH (20 eq), CH_3OH, 50° C, 14 h; H_3O^+, NH_4PF_6.

(iii) $HOCH_2C_6H_5$ (4eq), NaH (4 eq), THF, 40-50°C, 10 h; H_3O^+, NH_4PF_6.

(iv) $HSCH_2CO_2H$ (10 eq), NaH (10 eq), THF, RT, 36 h; H_3O^+, NH_4PF_6.

(v) H_2NCH_3 (400 eq), CH_2Cl_2, RT, 2 DAYS; H_3O^+, NH_4PF_6.

Scheme III



(i) $H_2C(CO_2R)_2$ (2eq), NaH (2 eq), THF, 40 - 50°C, 10 h; H_3O^+, NH_4PF_6.

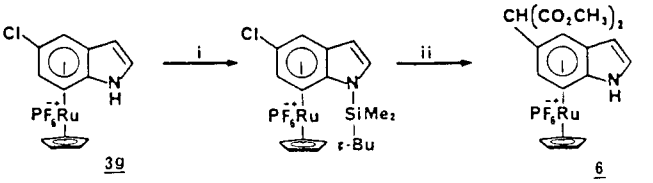
(ii) $HSCH_2CO_2H$ (10 eq), NaH (10 eq), THF, RT, 36 h; H_3O^+, NH_4PF_6.

(Rh, Ir, Co). But these results are quite compatible with the observed chemical shifts δ 6.6–5.3 of the isolobal neutral tricarbonylchromium complex.[26] The proton-decoupled ^{13}C NMR spectrum of complex **3b** shows a sizable upfield shift of six carbon atoms complexed to the CpRu unit. Similar observations have been reported with neutral (η^6-indole)$Cr(CO)_3$[26] and dicationic (η^6-indole)(η^5-C_5Me_5)M^{2+} (M = Rh, Ir, or Co) complexes.[20,21]

S_NAr Substitution of the Chloro Group of the (η^6-4- or η^6-5-Chloroindole)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphates. The method outlined in Scheme I allowed us to synthesize the 4- or 5-chloroindole complex **3e** or **3f** in excellent yields. These complexes are ideal substrates for effecting controlled functionalization of the aryl ring of the substituted indole[27] in a manner analogous to the nucleophilic displacement processes established for

(27) Moriarty, R. M.; Ku, Y. Y.; Gill, U. S. *J. Chem. Soc., Chem. Commun.* **1987**, 000.

Scheme IV



i: NaH/THF/t-BuSiMe$_2$Cl

ii: NaH/THF/$CH_2(CO_2CH_3)_2$; HCl/H_2O

(η^6-haloarene)(η^5-Cp)M(II) (M = Fe or Ru) complexes.[19a-c,28a,b,29a,b]

Complexes **3e** and **3f** were found to undergo smooth nucleophilic substituion of the chlorine atom with a range of carbon, sulfur, oxygen, and nitrogen nucleophiles to yield new complexes (Schemes II and III). The yields of the complexes **4a–f** and **5a–c** averaged about 80%, and their structures were determined by using high-resolution ^1H NMR, ^{13}C NMR, IR, and microanalytical data.

New reactions that lead to the formation of aryl–carbon bonds are of central importance in synthesis of indole derivatives. For this reason, we first studied reactions of complexes **3e** and **3f** with stabilized enolates $NaCH(CO_2CH_3)_2$ and $NaCH(CO_2C_2H_5)_2$.

New substituted indole complexes **4a,b** and **5a,b** were obtained in excellent yields. The ^1H NMR (400-MHz) spectrum of complex **4b** showed that the complexed aryl ring protons are markedly shifted upfield: δ (acetone-d_6) 7.19 (s, 4-H), 7.18 (d, 7-H, $J_{6,7}$ = 5 Hz), 6.18 (d, 6-H, $J_{6,7}$ = 5 Hz). The olefinic protons are shifted slightly downfield as compared to free ligand: δ 7.79 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 6.57 (d, 3-H), $J_{2,3}$ = 3.4 Hz). Complete NMR spectral data are given in the Experimental Section. The proton-decoupled ^{13}C NMR spectrum of complex **4b** showed a sizable upfield shift of the six carbon atoms complexed to the CpRu unit.

While these results indicated the feasibility of using the CpRu unit as an auxilliary unit in the formation of aryl–carbon bonds with 4- or 5-substituted *N*-methylindoles, there remained the problem of N_1 deprotection. We found that the *tert*-butyldimethylsilyl group can be used for this purpose and that it is conveniently removed during the HCl–aqueous workup (Scheme IV).

Reaction of complex **3e** with an excess of methanol in the presence of the 10 molar equiv of NaOH resulted in substitution of the chloro group, giving rise to (η^6-5-methoxy-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium hexafluorophosphate (**4c**) (Scheme II). Similar treatment of complex **3e** with a 20 M excess of phenyl methoxide (generated from benzyl alcohol and NaH) gave the corresponding novel complex **4d** (Scheme II) in excellent yield. It is noteworthy that even an aqueous solution (40%) of methylamine reacted with complex **3e** in THF at room temperature to give the desired substitution product **4f**. Analytical and spectral data for complexes **4c**, **4d**, and **4f** are given in the Experimental Section.

The above results establish the feasibility of introducing carbon, oxygen, and nitrogen nucleophiles at the 5- and

(28) (a) Lee, C. C.; Gill, U. S.; Iqbal, M.; Azogu, C. I.; Sutherland, R. G. *J. Organomet. Chem.* **1982**, *231*, 151. (b) Lee, C. C.; Aziz, A. S.; Chowdhury, R. L.; Gill, U. S.; Piorko, A.; Sutherland, R. G. *J. Organomet. Chem.* **1986**, *315*, 79.

(29) For S_NAr reaction upon (chlorobenzene)ruthenium complexes see: (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N.; Shul'pina, L. S. *Dokl. Akad. Nauk. SSSR* **1981**, 480. (b) Segal, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1338.

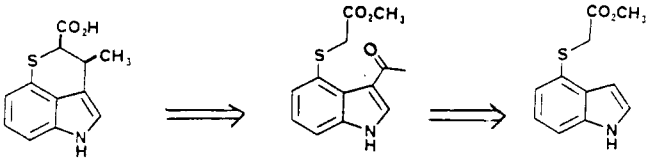
(30) Kozikowski, A. P.; Greco, M. N.; Springer, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 7622.

4-positions in complexes **3e** and **3f**, respectively. The potential synthetic utility of these procedures is also indicated by the fact that 4- or 5-(*S*)-((carboxymethyl)-thio)-*N*-methylindole complexes **5c** and **4e** were obtained from reactions of disodium salt of mercaptoacetic acid with complexes **3f** and **3e**, respectively.

An important step in the above method for organic synthesis is the release of the desired organic ligand from the organometallic complex. For example, ligand disengagement of complex **3g** was achieved by vacuum sublimation at 160–180 °C and as well as by photolysis in acetonitrile to produce 5-chloroindole in a good yield. A significant feature of the latter method is that the $[(CH_3CN)_3Ru(Cp)]PF_6$ (1) can be separated from the free ligand and recycled to **3g** by reaction with another substituted indole.

Conclusions

This work represents the first examples of ruthenium complexes of indole substrates. We also have demonstrated that S_NAr reactions in chloroindoles are possible via temporary complexation to the CpRu unit. The foregoing results show that S_NAr reaction upon CpRu-complexed 4- or 5-chloroindole is a synthetically useful process, particularly for indoles bearing substituents at the 4- or 5-position. Complex **5c** is suited for conversion to Kozikowski's[31] 4-sulfur-substituted indole free ligand in the synthesis of chuangxinmycin (**7**). In fact the *N*-methyl group is necessary in the formation of **5c**, and practically it would have to be removed for actual synthesis of **7**.



7

Experimental Section

^1H and ^{13}CNMR spectra were recorded by using Bruker WP-200 and 400 MHz spectrometers. Melting points were determined by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Microanalysis was performed by Microtech Labs, Skokie, IL. All reactions were performed under a nitrogen atmosphere by using standard techniques. Solvents were dried as follows: tetrahydrofuran (THF) from sodium benzophenone; 1,2-dichloroethane and acetonitrile from molecular sieves (4A).

(Cyclopentadienyl)tris(acetonitrile)ruthenium hexafluorophosphate, $[(Cp)Ru(CH_3CN)_3]PF_6$ (1), was prepared by photolysis of (η^6-benzene)(η^5-cyclopentadienyl)ruthenium hexafluorophosphate[24b] in acetonitrile according the literature procedure.[24a]

Synthesis of (η^6-Indole)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (3a). A solution of indole (280 mg, 2.4 mmol) in 20 mL of 1,2-dichloroethane was degassed for approximately 5 min with nitrogen, and $[CpRu(CH_3CN)_3]$ (891 mg, 2.0 mmol) was added. After the mixture was heated for 15 h at 40–50 °C under nitrogen, the solvent was removed by rotary evaporation and the residue was washed with ether (4 × 15 mL) to remove unreacted indole. The solid residue was redissolved in acetone, dried over Na_2SO_4, and decolorized with charcoal. After concentration of the acetone solution to about 3 mL, ether was added to precipitate 729 mg (85% yield) of complex **3a** which is a light yellow crystalline solid: mp 245–247 °C; ^1H NMR δ (acetone-d_6) 11.24 (s, NH), 7.83 (b s, 2-H), 7.10 (d, 7-H, $J_{6,7}$ = 2.4 Hz), 6.98 (d, 4-H, $J_{4,5}$ = 2.2 Hz), 6.55 (b s, 3-H), 5.94 (d, 6-H, $J_{5,6}$ = 2.4 Hz), 5.89 (d, 5-H, $J_{5,6}$ = 2.4 Hz), 4.96 (s, Cp); ^{13}C NMR δ (acetone-d_6) 137.84 (C-2), 103.79 (C-3), 110.51, 97.17, 81.74, 81.60, 78.39, 72.14 (C_6 ring), 79.09 (Cp). Anal. Calcd for $C_{13}H_{12}NRuPF_6$: C, 36.46; H, 2.82. Found: C, 36.46; H, 2.84.

Complexes **3b–g** were obtained by using a similar procedure. Yields and spectroscopic and analytical data are given in the following.

(η^6-*N*-Methylindole)(η^5-cyclopentadienyl)ruthenium hexafluorophosphate (3b): yield 89%; mp 192–194 °C; ^1H NMR δ (acetone-d_6) 7.73 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 7.09 (d, 7-H, $J_{6,7}$ = 6.0 Hz), 7.00 (d, 4-H, $J_{4,5}$ = 5.8 Hz), 6.53 (d, 3-H, $J_{2,3}$ = 3.4 Hz), 5.98 (t, 6-H, J = 5.6 Hz), 5.94 (t, 5-H, J = 5.7 Hz), 5.03 (s, Cp), 3.82 (s, NCH_3); ^{13}C NMR δ (acetone-d_6) 142.05 (C-2), 103.49 (C-3), 111.04, 97.45, 81.77, 81.32, 70.43 (C_6 ring), 78.90 (Cp), 33.26 (N-CH_3). Anal. Calcd for $C_{14}H_{14}NRuPF_6$: C, 38.02; H, 3.12. Found: C, 38.05; H, 3.15.

(η^6-5-Methyl-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium hexafluorophosphate (3c): yield 88%; mp 223–225 °C; ^1H NMR δ (acetone-d_6) 7.70 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 7.04 (d, 7-H, $J_{6,7}$ = 6.2 Hz), 7.03 (s, 4-H), 6.50 (d, 3-H, $J_{2,3}$ = 3.4 Hz), 6.00 (d, 6-H, $J_{6,7}$ = 6 Hz), 5.02 (s, Cp), 3.79 (s, NCH_3), 2.38 (s, $ArCH_3$); ^{13}C NMR δ (acetone-d_6) 142.10 (C-2), 103.21 (C-3), 110.44, 97.85, 97.32, 82.71, 80.11 60 (C_6-ring), 79.26 (Cp), 33.27 (N-CH_3), 20.42 ($ArCH_3$). Anal. Calcd for $C_{15}H_{16}NRuPF_6$: C, 39.48; H, 3.53. Found: C, 39.37; H, 3.50.

(η^6-5-Bromoindole)(η^5-cyclopentadienyl)ruthenium hexafluorophosphate (3d): yield 80%; mp 146–148 °C; ^1H NMR δ (acetone-d_6) 7.93 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 7.55 (s, 4-H), 7.30 (d, 7-H, J = 6 Hz), 6.62 (d, 3-H, $J_{2,3}$ = 3.4 Hz), 6.48 (d, 6-H, J = 6 Hz); ^{13}C NMR δ (acetone-d_6) 139.18 (C-2), 103.40 (C-3), 109.82, 98.01, 86.24, 85.60, 82.16, 72.62 (C_6 ring), 81.57 (Cp). Anal. Calcd for $C_{13}H_{11}BrNRuPF_6$: C, 30.79; H, 2.18. Found: C, 31.02; H, 2.15.

(η^6-5-Chloro-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium hexafluorophosphate (3e): yield 83%; mp 211–213 °C; ^1H NMR δ (acetone-d_6) 7.84 (d, 2-H, $J_{2,3}$ = 3.2 Hz), 7.50 (s, 4-H), 7.29 (d, 7-H, $J_{6,7}$ = 6.5 Hz), 6.60 (d, 3-H), $J_{2,3}$ = 3.2 Hz), 6.48 (d, 6-H, $J_{6,7}$ = 5.8 Hz), 5.21 (s, Cp), 3.87 (s, NCH_3); ^{13}C NMR δ (acetone-d_6) 143.30 (C-2), 103.11 (C-3), 110.20, 97.46, 86.95, 82.95, 80.12, 70.19 (C_6 ring), 81.13 (Cp), 33.55 (NCH_3). Anal. Calcd for $C_{14}H_{13}ClNRuPF_6$: C, 35.27; H, 2.75; Cl, 7.44. Found: C, 35.41, H, 2.62; Cl, 7.41.

(η^6-4-Chloro-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium hexafluorophosphate (3f): yield 85%; mp 185–187 °C; ^1H NMR δ (acetone-d_6) 7.98 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 7.18 (d, 7-H, $J_{6,7}$ = 5.6 Hz), 6.73 (d, 3-H, $J_{2,3}$ = 3.4 Hz), 6.48 (d, 5-H, $J_{6,7}$ = 5.6 Hz), 6.15 (t, 6-H, $J_{6,7}$ = 5.7 Hz), 5.17 (s, Cp), 3.92 (s, NCH_3); ^{13}C NMR δ (acetone-d_6) 143.28 (C-2), 101.59 (C-3), 110.10, 98.50, 97.10, 83.46, 81.11, 70.73 (C_6 ring), 80.94 (Cp), 33.83 (NCH_3). Anal. Calcd for $C_{14}H_{13}ClNRuPF_6$: C, 35.27; H, 2.75; Cl, 7.44. Found: C, 35.06; H, 2.76; Cl, 7.41.

(η^6-5-Chloroindole)(η^5-cyclopentadienyl)ruthenium hexafluorophosphate (3g): yield 80%; mp 156–158 °C; ^1H NMR δ (acetone-d_6) 7.94 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 7.49 (d, 4-H, $J_{4,6}$ = 1.2 Hz), 7.30 (d, 7-H, $J_{6,7}$ = 5.8 Hz), 6.63 (d, 3-H, $J_{2,3}$ = 3.4 Hz), 6.44 (d, 6-H, $J_{6,7}$ = 5.2 Hz), 5.15 (s, Cp). Anal. Calcd for $C_{13}H_{11}ClNRuPF_6$: C, 33.74; H, 2.40. Found: C, 33.63; H, 2.39.

Nucleophilic Displacement Reactions Using Carbon Nucleophiles. The general procedure is illustrated for the reaction of complex **3e** with $NaCH(CO_2CH_3)_2$.

Synthesis of (η^6-5-(Dicarbomethoxymethyl)-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (4a). To a degassed solution containing the carbanion prepared from the reaction between dimethyl malonate (0.23 mL, 2.0 mmol) and NaH (48 mg, 2.0 mmol) in THF at room temperature was added complex **3e** (477 mg, 1.0 mmol). After being heated under reflux overnight under nitrogen, the reaction mixture was quenched with 10% HCl followed by addition of an aqueous solution of NH_4PF_6 (326 mg, 2.0 mmol). The THF was then removed by rotary evaporation. The residue was extracted with CH_2Cl_2 (3 × 30 mL), and the combined CH_2Cl_2 extracts were dried over $NaSO_4$. The solvent was removed by rotary evaporation, and the residue was washed with ether (3 × 15 mL) to remove unreacted dimethyl malonate. The resulting solid was crystallized from acetone/ether to give 510 mg (88% yield) of complex **4a** as pale yellow crystalline solid **4a**: mp 215–217 °C; ^1H NMR δ (acetone-d_6) 7.83 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 7.23 (s, 4-H), 7.21 (d, 7-H, $J_{6,7}$ = 6.4 Hz), 6.60 (d, 3-H, $J_{2,3}$ = 3.4 Hz), 6.19 (d, 6-H, $J_{6,7}$ = 6.4 Hz), 5.04 (s, Cp), 3.88 (s, CO_2CH_3), 3.84 (s, NCH_3), 3.82 (s,

(31) Liang, H.-T.; Hsu, H.-D.; Chang, C. P.; Ku, H.-E. *Chem. Abstr.* **1976**, *34*, 129.

CO_2CH_3); ^{13}C NMR δ (acetone-d_6) 167.91, and 167.87 (CO's), 142.81 (C-2), 103.47 (C-3), 111.03, 97.31, 93.15, 82.67, 79.82, 70.22 (C_6 ring), 80.02 (Cp), 53.68, 53.65 (CO_2CH_3's), 55.75 (CH), 33.42 (NCH_3). Anal. Calcd for $C_{19}H_{20}NO_4RuPF_6$: C, 39.80; H, 3.51. Found: C, 39.92; H, 3.50.

Synthesis of (η^6-4-(Dicarbomethoxymethyl)-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (5a). Complex **5a** was obtained from complex **3f** following the above procedure. Yield, spectroscopic, and analytical data are the following: yield 86%; mp 143–145 °C; ^1H NMR δ (acetone-d_6) 7.80 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 7.14 (d, 7-H), $J_{6,7}$ = 6 Hz), 6.69 (d, 3-H), $J_{2,3}$ = 3.4 Hz), 6.14 (d, 5-H), $J_{5,6}$ = 5.6 Hz), 6.05 (t, 6-H, $J_{6,7}$ = 5.8 Hz), 5.41 (s, CH), 4.99 (s, Cp), 3.92 (s, CO_2CH_3), 3.82 (s, NCH_3), 3.77 (s, CO_2CH_3); ^{13}C NMR δ (acetone-d_6) 167.79, 167.62 (CO's), 142.49 (C-2), 101.88 (C-3), 110.52, 98.39, 89.57, 82.36, 81.11, 70.29 (C_6 ring), 79.98 (Cp), 54.56 (CH), 53.73 (CO_2CH_3), 33.52 (NCH_3). Anal. Calcd for $C_{19}H_{20}NO_4RuPF_6$: C, 39.80; H, 3.52. Found: C, 40.02; H, 3.50.

Synthesis of (η^6-5-(Dicarbethoxymethyl)-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (4b). The reaction of the carbanion generated from diethyl malonate with complex **3e** was carried out as above. Complex **4d** was obtained as a yellow crystalline solid in 75% yield: mp 166–168 °C; ^1H NMR δ (acetone-d_6) 7.79 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 7.19 (s, 4-H), 7.18 (d, 7-H, $J_{6,7}$ = 5.0 Hz), 6.57 (d, 3-H, $J_{2,3}$ = 3.4 Hz), 6.18 (d, 6-H, $J_{6,7}$ = 5.0 Hz), 4.83 (s, CH), 5.02 (s, Cp), 4.24–4.34 (m, $CO_2CH_2CH_3$), 3.85 (s, NCH_3), 1.25–1.31 (m, $CO_2CH_2CH_3$); ^{13}C NMR δ (acetone-d_6) 167.44 (CO), 142.77 (C-2), 103.49 (C-3), 111.03, 97.35, 93.250, 82.67, 79.84, 70.24 (C_6 ring), 79.99 (Cp), 63.12 ($CO_2CH_2CH_3$), 56.16 (CH), 33.41 (NCH_3), 14.22 ($CO_2CH_2CH_3$). Anal. Calcd for $C_{21}H_{24}NO_4RuPF_6$: C, 42.01; H, 4.03. Found: C, 41.95; H, 4.04.

Synthesis of (η^6-4-(Dicarbethoxymethyl)-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (5b). A similar procedure described above was used in the reaction between complex **3f** and the carbanion generated from diethyl malonate to give complex **5b**. Yield, spectroscopic, and analytical data are as follows: yield 80%; mp 145–147 °C; ^1H NMR δ (acetone-d_6) 7.80 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 7.14 (d, 7-H), $J_{6,7}$ = 6 Hz), 6.69 (d, 3-H, $J_{2,3}$ = 3.4 Hz), 6.15 (d, 5-H, $J_{5,6}$ = 5.6 Hz), 6.05 (t, 6-H, J = 5.7 Hz), 5.36 (s, CH), 5.00 (s, Cp), 4.37–4.40 (m, 2 H), 4.23–4.26 (m, 2 H), two types of CH_2's, 3.83 (s, NCH_3), 1.35 (t, $CO_2CH_2CH_3$), J = 7.0 Hz), 1.24 (t, $CO_2CH_2CH_3$, J = 7.0 Hz), two types of CH_3's; ^{13}C NMR δ (acetone-d_6) 167.28, 167.14 (CO's), 142.44 (C-2), 101.95 (C-3), 110.56, 98.39, 89.63, 82.33, 81.14, 70.26 (C_6 ring), 79.97 (Cp), 63.29, 63.13 ($CO_2CH_2CH_3$), 54.99 (CH), 33.51 (N-CH_3), 14.33, 14.23 ($CO_2CH_2CH_3$). Anal. Calcd for $C_{21}H_{24}NO_4RuPF_6$: C, 42.01; H, 4.03. Found: C, 41.85; H, 3.92.

Reactions of Complexes 3e and 3f with Heteroatom Nucleophiles. Synthesis of (η^6-5-((*S*)-(Carboxymethyl)thio)-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (4e). Complex **3e** (239 mg, 0.5 mmol) was added as a solid to a solution containing the disodium salt of mercaptoacetic acid prepared from the reaction between mercaptoacetic acid (461 mg, 5.0 mmol) and NaH (240 mg, 10.0 mmol) in 20 mL of the THF at 0 °C. The reaction mixture was stirred for 36 h at room temperature under nitrogen and then was quenched with 10% HCl followed by addition of an aqueous solution of NH_4PF_6 (326 mg, 2.0 mmol). After the THF was removed by rotary evaporation, the residue was extracted with CH_2Cl_2 (4 × 30 mL), the combined extracts were dried over Na_2SO_4 and the solution was concentrated to a small volume (2–3 mL). Ether was added to give 188 mg (70% yield) of complex **4e** as yellow crystalline solid: mp 186–188 °C; ^1H NMR δ (acetone-d_6) 7.77 (d, 2-H), $J_{2,3}$ = 3.4 Hz), 7.30 (s, 4-H), 7.17 (d, 7-H, $J_{6,7}$ = 5.6 Hz), 6.55 (d, 3-H, $J_{2,3}$ = 3.4 Hz), 6.24 (dd, 6-H, $J_{6,7}$ = 5.6 Hz), 5.10 (s, Cp), 3.90 (s, CH_2CO_2H), 3.82 (s, NCH_3); ^{13}C NMR δ (acetone-d_6) 170.40 (CO), 142.81 (C-2), 103.20 (C-3), 110.46, 98.77, 97.59, 83.54, 80.92, 70.24 (C_6 ring), 80.36 (Cp), 37.56 (CH_2CO_2H), 33.45 (NCH_3). Anal. Calcd for $C_{16}H_{16}NO_2SRuPF_6$: C, 36.10; H, 3.03; S, 6.02. Found: C, 36.06; H, 2.99; S, 6.03.

Synthesis of (η^6-4-((*S*)-(Carboxymethyl)thio)-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium hexafluorophosphate (5c): yield 72%; mp 185–187 °C; ^1H NMR δ (acetone-d_6) 7.90 (d, 2-H, $J_{2,3}$ = 3.5 Hz), 7.13 (d, 7-H, $J_{6,7}$ = 5.7 Hz), 6.73 (d, 3-H, $J_{2,3}$ = 3.5 Hz), 6.30 (d, 5-H, $J_{5,6}$ = 5.6 Hz), 6.11 (t, 6-H, J = 5.7 Hz), 5.09 (s, Cp), 4.07 (s, CH_2CO_2H), 3.89 (s, NCH_3); ^{13}C NMR δ (acetone-d_6) 170.13 (CO), 142.42 (C-2), 102.33 (C-3), 110.22, 99.50, 95.248 83.66, 81.22, 69.85 (C_6 ring), 80.19 (Cp), 36.79 (CH_2CO_2H), 33.64 (N-CH_3). Anal. Calcd for $C_{16}H_{16}NO_2SRuPF_6$: C, 36.10; H, 3.03; S, 6.02. Found: C, 36.06; H, 2.99; S, 6.03.

Synthesis of (η^6-5-Methoxy-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (4c). Complex **3e** (239 mg, 0.5 mmol) was added as a solid to a methanol solution containing NaOH (400 mg, 10 mmol) in 20 mL of methanol. The reaction mixture was heated under reflux for 14 h under N_2 and then was neutralized with 10% HCl. Most of the MeOH was removed by rotary evaporation, and the aqueous residue was extracted with CH_2Cl_2 (3 × 30 mL). The combined CH_2Cl_2 extracts were dried over $MgSO_4$ and concentrated to 2–5 mL. Addition of ether yielded 205 mg (85% yield) of complex **4c** as a yellow crystalline solid: mp 223–225 °C; ^1H NMR δ (acetone-d_6) 7.71 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 7.12 (s, 4-H), 7.04 (d, 7-H, $J_{6,7}$ = 6.4 Hz), 6.49 (d, 3-H), $J_{2,3}$ = 3.4 Hz), 6.08 (d, 6-H, $J_{6,7}$ = 6.4 Hz), 5.09 (s, Cp), 3.85 (s, $ArOCH_3$), 3.79 (s, NCH_3); ^{13}C NMR δ (acetone-d_6) 142.53 (C-2), 103.38 (C-3), 131.82, 103.10, 88.60, 70.72, 67.89, 67.45 (C_6-ring), 78.96 (Cp), 57.75 (OCH_3), 33.44 (NCH_3). Anal. Calcd for $C_{15}H_{15}NORuPF_6$: C, 38.14; H, 3.14. Found: C, 38.24;, H, 3.29.

Synthesis of (η^6-5-(Methylamino)-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (4f). A mixture of complex **3e** (239 mg, 0.5 mmol) and methylamine (15 mL, 200 mmol) (40% aqueous solution) in 20 mL of the THF was stirred at room temperature for 2 days. The solution was taken to dryness by rotary evaporation. The residue was redissolved in CH_2Cl_2, an aqueous solution of NH_4PF_6 (163 mg, 1 mmol) was added, and the mixture was stirred for 10 min. The product was extracted with CH_2Cl_2 (2 × 25 mL). The combined extracts were dried over $NaSO_4$ and concentrated to a small volume (2–3 mL). Ether was added, the product was precipitated out, and 145 mg (60% yield) of complex **4f** was obtained: mp 143–145 °C; ^1H NMR δ (acetone-d_6) 7.59 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 6.84 (d, 7-H, $J_{6,7}$ = 6.3 Hz), 6.64 (s, 4-H), 6.41 (d, 3-H, $J_{2,3}$ = 3.4 Hz), 5.65 (d, 6-H, $J_{6,7}$ = 6.3 Hz), 4.94 (s, Cp), 3.72 (s, N-CH_3), 2.77 (d, $NHCH_3$, J = 5.2 Hz); ^{13}C NMR δ (acetone-d_6) 141.48 (C-2), 103.48 (C-3), 123.56, 108.15, 95.79, 67.13, 65.70, 62.09 (C_6-ring), 77.89 (Cp), 33.24 (NCH_3), 30.95 ($NHCH_3$).

Synthesis of (η^6-5-(Benzyloxy)-*N*-methylindole)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (4d). A mixture of benzyl alcohol (0.2 mL, 2.0 mmol) and NaH (48 mg, 2.0 mmol) in 20 mL of THF was stirred under N_2 for 10 min. To the mixture complex **3e** (239 mg, 0.5 mmol) was added as a solid. The reaction mixture was heated at 45–50 °C under reflux for 12 h and then quenched with 10% HCl. The usual workup gave complex **4d** (203 mg, 73%): mp 162–164 °C; ^1H NMR δ (acetone-d_6) 7.39–7.53 (m, uncomplexed C_6 ring), 7.74 (d, 2-H, $J_{2,3}$ = 6.8 Hz), 7.22 (d, 4-H, J = 3 Hz), 7.07 (d, 7-H), $J_{6,7}$ = 13 Hz), 6.52 (d, 3-H, $J_{2,3}$ = 6.8 Hz), 6.19, 6.16 (dd, 6-H, $J_{4,6}$ = 3 Hz, $J_{6,7}$ = 13 Hz) 5.17 (s, $CH_2C_6H_5$), 5.03 (s, Cp), 3.79 (s, NCH_3); ^{13}C NMR δ (acetone-d_6) 136.35, 129.49, 1129.38, 128.97 (uncomplexed C_6 ring), 142.57 (C-2), 103.39 (C-3), 130.70, 109.45, 96.15, 72.74, 71.29, 68.11 (C_6 ring), 79.14 (Cp), 68.02 ($CH_2C_6H_5$), 33.44 (NCH_3). Anal. Calcd for $C_{21}H_{20}NORuPF_6$: C, 45.91; H, 3.67. Found: C, 45.33; H, 3.52.

Synthesis of (η^6-5-(Dicarbomethoxymethyl)indole)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (6) Using the *tert*-Butyldimethylsilyl N-Protecting Group. A mixture of complex **3e** (200 mg, 0.43 mmol) and NaH (14 mg, 0.65 mmol) in THF (20 mL) was stirred for 20 min at room temperature under N_2. To the mixture was added *tert*-butyldimethylsilyl chloride (85 mg, 0.65 mmol). The mixture changed color from red-orange to brownish green. The reaction mixture was stirred for another 20 min and then was transferred with a syringe to another flask containing sodium salt of dimethyl malonate [generated from the reaction between NaH (104 mg, 4.3 mmol) and dimethyl malonate (0.5 mL, 4.3 mmol) at room temperature in THF (10 mL) for 5 min]. The reaction mixture was heated under reflux for 15 h. After the usual workup complex **6** was obtained (192 mg, 80%): mp 188–190 °C; ^1H NMR δ (acetone-d_6) 7.89 (d, 2-H, $J_{2,3}$ = 3.4 Hz), 7.20 (d, 7-H, $J_{6,7}$ = 6.3 Hz), 7.18 (s, 4-H), 6.59 (d, 3-H, $J_{2,3}$ = 3.4 Hz), 6.16 (d, 6-H, $J_{6,7}$ = 6.3 Hz), 4.96 (s, Cp), 4.85 (s, CH), 3.83 (s), 3.79 (s), two CO_2CH_3's; ^{13}C NMR δ (acetone-d_6) 167.9, 167.87 (CO's), 138.72 (C-2), 103.90 (C-3), 110.55, 97.19, 93.23, 83.00, 79.49, 71.97 (C_6 ring), 80.37 (Cp), 56.81

(CH), 53.66 (CO_2CH_3). Anal. Calcd for $C_{18}H_{18}NO_4RuPF_6$: C, 39.5; H, 3.31. Found: C, 38.33; H, 3.12.

Decomplexation Reactions. A 463-mg (1.0 mmol) sample of complex **3g** was dissolved in acetone and transferred to a vacuum sublimator. The solution was dried to a thin film using a N_2 stream. The sample was heated under vacuum (10 mm) at 165–170 °C (oil bath) for 2 h. The material from the cold finger was dissolved in chloroform. After removal of chloroform, the solid residue (135 mg, 89%) was identified on the basis of ^1H NMR spectral analysis and melting point to be 5-chloroindole.

In another experiment, 463 mg (1.0 mmol) of complex **3g** in 30 mL of CH_3CN was photolyzed for 12 h. After evaporation of the acetonitrile by rotary evaporation, the solid residue was washed with ether (3 × 30 mL). The combined ether extracts were dried over $MgSO_4$, and the solvent was removed to give a solid residue (139 mg, 92%) that was identified on the basis of ^1H NMR spectral analysis and melting point to be 5-chloroindole.

Acknowledgment. We thank the Office of Naval Research for support of this work under Contract ONR 83K-0306.

Registry No. 1, 80049-61-2; **3a**, 112398-42-2; **3b**, 112398-44-4; **3c**, 112398-46-6; **3d**, 112398-48-8; **3e**, 112398-50-2; **3f**, 112398-52-4; **3g**, 112398-54-6; **4a**, 112398-56-8; **4b**, 112398-60-4; **4c**, 112398-68-2; **1d**, 112398-72-8; **4e**, 112398-64-8; **4f**, 112398-70-6; **5a**, 112398-58-0; **5b**, 112398-62-6; **5c**, 112398-66-0; **6**, 112398-74-0; $NaCH(CO_2CH_3)_2$, 18424-76-5; indole, 120-72-9; 1-methylindole, 603-76-9; 1,5-dimethylindole, 27816-53-1; 5-bromoindole, 10075-50-0; 5-chloro-1-methylindole, 112398-75-1; 4-chloro-1-methylindole, 77801-91-3; 5-chloroindole, 17422-32-1; sodium mercaptoacetate, 16023-01-1; dimethyl malonate, 108-59-8; diethyl malonate, 105-53-3.

Molecular Orbital Study of Bimetallic Complexes Containing Conjugated and Aromatic Hydrocarbons as Bridging Ligands

Longgen Zhu and Nenad M. Kostić*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received July 6, 1987

Nonparametrized molecular orbital calculations were carried out on 14 compounds of the type $Pd_2L_2(\mu\text{-A})(\mu\text{-B})$ containing PH_3 or Cl^- as terminal ligands L and Br^-, $C_3H_5^-$, C_4H_6, $C_5H_5^-$, and C_6H_6 as bridging ligands A and B. These compounds provide the first examples of coordination of two metal atoms to the same side of planar, conjugated organic ligands. Since $Pd_2L_2(\mu\text{-A})$ fragment has only two low-lying vacant molecular orbitals, it acts as a four-electron acceptor even toward $C_5H_5^-$ and C_6H_6, ligands that usually are six-electron donors. Coordination of these rings in the bimetallic complexes results in partial localization of the π electrons, i.e., in diminution of the π conjugation. This effect of bridging coordination is especially prominent in the $C_5H_5^-$ ring, which becomes akin to a composite of a coordinated allyl ligand (a four-electron donor) and an uncoordinated olefin fragment. If such partial localization of π electrons occurs in aromatic molecules chemisorbed on the metal surface, as it does in the molecules coordinated in the bimetallic complex, this effect may perhaps be related to the high efficiency with which palladium metal catalyzes hydrogenation of arenes.

Introduction

Transition metals form myriad of monometallic complexes with allyl, butadiene, cyclopentadienyl, and benzene ligands and with various derivatives of these hydrocarbons. Although bimetallic compounds with conjugated hydrocarbons as bridging ligands are still rare,[1] triple-decker sandwiches[2,3] and pentadienyl complexes[4-6] being perhaps the best-known examples, the interest in them is growing. The subject of this theoretical study are dipalladium complexes in which the metal atoms are coordinated to the same face of the π ligand, as shown in Chart I. The actual compounds can be half-sandwiches, containing one π ligand, or sandwiches, containing two similar or dissimilar π ligands.

These noteworthy compounds are of recent vintage. Although $Pd_2(Al_2Cl_7)_2(\mu\text{-}C_6H_6)_2$ was reported in 1965[7] and the homologous $Pd_2(AlCl_4)_2(\mu\text{-}C_6H_6)_2$ was reported in 1970,[8] systematic investigation of such complexes containing bridging multihapto hydrocarbon ligands did not begin until mid-1970s.[9] Similar complexes of nickel have recently been discovered.[10] The new compounds are significant not only because of their novelty but also be-

Chart I

Table I. Complexes of the Type $H_3P\text{-}(A)\overline{Pd\text{-}Pd}(B)\text{-}PH_3$ That Are Examined by Molecular Orbital Calculations[a,b]

	A			
B	Br^-	$C_3H_5^-$	$C_5H_5^-$	C_6H_6
Br^-	O	O		
$C_3H_5^-$	X[c]	X	X	O
C_4H_6	O	O	O	O[d]
$C_5H_5^-$	X	X	X	
C_6H_6	O	O	O	X[d]

[a] The molecules are constructed from the fragments $Pd_2(PH_3)_2(\mu\text{-A})$ and B. [b] O, complex included in the study. X, existing complex with the given bridging ligands A and B, although with other terminal ligands than PH_3. [c] Existing with Cl^- and I^- as A. [d] Also calculated with Cl^- in the place of PH_3.

(1) Nesmeyanov, A. N.; Rybinskaya, M. I.; Rybin, L. V.; Kaganovich, V. S. *J. Organomet. Chem.* **1973**, *47*, 1.
(2) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 1.
(3) Siebert, W. *Nachr. Chem. Tech. Lab.* **1977**, *25*, 597.
(4) Rienäcker, R.; Yoshiura, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 677.
(5) Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 678.
(6) Böhm, M. C.; Gleiter, R. *Chem. Phys.* **1982**, *64*, 183.
(7) Allegra, G.; Immirzi, A.; Porri, L. *J. Am. Chem. Soc.* **1965**, *87*, 1394.
(8) Allegra, G.; Casagrande, G. T.; Immirzi, A.; Porri, L.; Vitulli, G. *J. Am. Chem. Soc.* **1970**, *92*, 289.
(9) Werner, H. *Adv. Organomet. Chem.* **1981**, *19*, 155. Section VI of this review deals with bonding.
(10) Hanko, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 704.

0276-7333/88/2307-0665$01.50/0