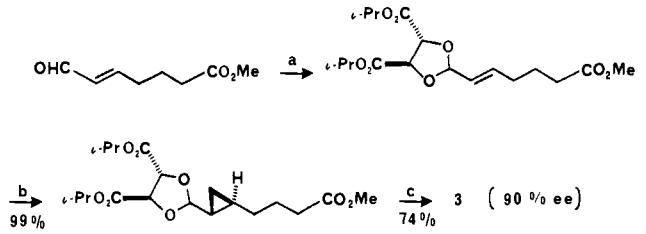
Scheme II[a]

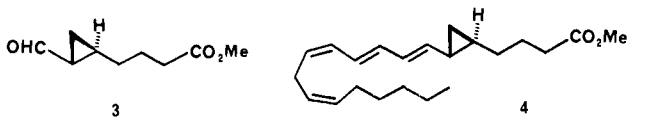


[a] (a) (1) $HC(OEt)_3$-EtOH, NH_4NO_3, 78%, (2) L-(+)-DIPT, TsOH-Py 50%; (b) CH_2I_2-Et_2Zn; (c) TsOH, MeOH-H_2O.

(*c* 1.03, EtOH); IR (neat) 3000 (s), 2960 (m), 1755 (s), 1620 (m), 1380 (m), 1160 (w), 870 (w), 760 (m); ^1H NMR (CCl_4) δ 0.67-1.87 (m, 3 H), 1.27, 1.30 (2 t, J = 8 Hz, 3 H each), 1.87-2.37 (m, 1 H), 4.20 (q, J = 8 Hz, 4 H), 4.47-4.67 (m, 2 H), 5.03 (d, J = 5.6 Hz, 1 H), 7.07 (br s, 5 H, Ar H). Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.7; H, 6.6. Found: C, 64.7; H, 6.6.[8]

The observed selectivity is ascribed to the high affinity of the zinc reagent for ethereal oxygen. Complex formation between the oxygen atom and the organozinc reagent, followed by methylene transfer to the nearest face of the neighboring double bond, has been proposed to account for the stereoselectivity and the large rate enhancement found for methylene addition to allylic alcohols and ethers relative to simple olefins.[9,10]

It seems clear that the method described herein will be useful for the production of a wide range of chiral cyclopropanes, an increasingly important class of biologically active functionalities. One attractive initial target was the aldehyde **3**, a key intermediate in synthesis of 5,6-methanoleukotriene A_4 (**4**), a stable and selective



inhibitor of leukotriene biosynthesis.[11] An enantioselective synthetic route of **3** is shown in Scheme II.[12]

Acknowledgment. Financial supports from the Ministry of Education, Japanese Government, and generous gift sample from Ono Pharmaceutical Co. are acknowledged.

(8) The acetal group was transformed to the aldehyde or to the carboxylic acid as follows: A mixture of the acetal **2** (1.67 g, 5.0 mmol) and *p*-TsOH (1.0 g) in THF-water (50 mL-10 mL) was heated at reflux for 7 h. Usual workup followed by column chromatography on silica gel gave a colorless oil (450 mg, 62%): bp (bath temp) 120 °C (1 torr); $[\alpha]^{25}_D$ -378° (*c* 0.374, $CHCl_3$),[1c] $[\alpha]^{25}_D$-340° (*c* 0.363, $CHCl_3$); ^1H NMR (CCl_4) δ 1.17-2.77 (m, 4 H), 7.10 (m, 5 H), 9.33 (d, J = 3.8 Hz, 1 H); IR (neat) 3040 (w), 2850 (w), 2730 (w), 1695 (s), 1170 (m), 760 (m), 700 (m) cm^{-1}. Similarly the acetals **5** and **6** (entry 8 and 9 of Table I) were transformed to the corresponding aldehydes on treatment with *p*-TsOH in ethanol-water (1:1) at room temperature for 2-5 days in 75-79% yields. A solution of the acetal **2** (1.67 g, 5.0 mmol) in CCl_4 (50 mL) was oxidized with excess ozone at 0 °C for 5 h. The solvent was evaporated in vacuo and the residue was dissolved in ethyl acetate and washed with brine. The separated organic layers were dried over sodium sulfate and concentrated in vacuo. The residue was dissolved in EtOH-10 N KOH (25 mL-5 mL) and the mixture was stirred at 0 °C for 2 h to complete the hydrolysis of the ester. The mixture was poured in cold 2 N HCl and the product was extracted with ethyl acetate repeatedly. After drying and concentration of the organic layers, the product was purified by column chromatography on silica gel to give 2-phenylcyclopropanecarboxylic acid as a colorless liquid (0.435 g, 43% in two steps overall yield): see legend f of Table I. Similarly the ozonolysis of the acetal of entry 3, Table I, gave the corresponding ester in 67% yield.

(9) Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Org. React.* **1973**, *20*, 1.

(10) Poulter, C. D.; Friedrich, E. C.; Winstein, S. *J. Am. Chem. Soc.* **1969**, *91*, 6892.

(11) Nicolaou, K. C.; Petasis, N. A.; Seitz, S. P. *J. Chem. Soc., Chem. Commun.* **1981**, 1195.

(12) Stereochemical purity (90% ee) of the product was determined by the following conversion: Treatment of **6** with (2*R*,4*R*)-2,4-pentandiol and pyridinium tosylate in benzene at reflux for 1 h gave the corresponding acetal (87% yield): $[\alpha]^{27}_D$ -51.2° (*c* 1.05, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.31 (d, J = 5.65 Hz, $CH(OR)_2$); the *S* isomer δ 4.35 (d, J = 5.65 Hz).

Homochiral Ketals in Organic Synthesis. Diastereoselective Cyclopropanation

Eugene A. Mash* and Keith A. Nelson

Department of Chemistry, University of Arizona Tucson, Arizona 85721

Received July 8, 1985

The modern synthetic chemist often plans an *asymmetric* synthesis of a complex target molecule. Incorporation of one or more protecting groups is usually an integral part of this plan. Although the number of available protecting groups has grown as the complexity of target molecules has increased, on the whole protecting groups remain unidimensional: they protect, nothing more.[1] This situation is unfortunate given the time and effort devoted to their manipulation. Development of methodology for asymmetric synthesis based on incorporation of *homochiral protecting groups* would seem both logical and economical.[2,3] We have embarked on such a developmental program, and herein report that homochiral cycloalkenone ketals undergo efficient and diastereoselective cyclopropanation when treated with the Simmons-Smith reagent.[4,5]

Treatment of 2-cyclohexen-1-one ketal **1**[6] (2.5 mmol) with freshly prepared zinc-copper couple[7] (1.63 g), methylene iodide (8 mmol), and a crystal of iodine in refluxing diethyl ether gave, after 1 h and in 90-98% chemical yield, a 9:1 mixture of diastereomeric cyclopropanes **2a** and **2b**,[6] as determined by 62.9-MHz ^{13}C NMR spectroscopy.[8] This ratio was confirmed and the identity of the major diastereomer established by hydrolysis[9] of the diastereomeric mixture to (1*R*,6*S*)-bicyclo[4.1.0]heptan-2-one, $[\alpha]^{25}_D$ +12.7° (*c* 3.4, $CHCl_3$), the rotation of which corresponds to 83% optical purity.[5a,c] Most encouragingly, 2-cyclopenten-1-one ketal **3** and 2-cyclohepten-1-one ketal **5** gave similar results[9,10]

(1) Green, T. W. "Protective Groups in Organic Synthesis"; Wiley: New York, 1981.

(2) Recently, diastereoselective β-addition reactions of homochiral acetals and ketals have been described; see: (a) Fujiwara, J.; Fukutani, Y.; Hasegawa, M.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1984**, *106*, 5004-5005. (b) Fukutani, Y.; Maruoka, K.; Yamamoto, H. *Tetrahedron Lett.*; **1984**, 5911-5912. (c) Ghribi, A.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1984**, 3083-3086.

(3) Other synthetic uses for homochiral acetals and ketals have been described; see: (a) Elliott, J. D.; Steele, J.; Johnson, W. S. *Tetrahedron Lett.* **1985**, 2535-2538 and previous articles in the series. (b) Mori, A.; Fujiwara, J.; Maruoka, K.; Yamamoto, H. *Tetrahedron Lett.* **1983**, 4581-4584. (c) Sekizaki, H.; Jung, M.; McNamara, J. M.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 7372-7374.

(4) For reviews of the Simmons-Smith reaction, see: (a) Furukawa, J.; Kawabata, N. In "Advances in Organometallic Chemistry"; Stone, F. G. A., West, R., Ed.; Academic Press: New York, 1974; Vol. 12, Chapter 3. (b) Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Org. React.* **1972**, *20*, 1-131.

(5) Previous uses of the Simmons-Smith reaction to produce homochiral cyclopropanes include: (a) Johnson, C. R.; Barbachyn, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 4290-4291. (b) Lightner, D. A.; Jackman, D. E. *Tetrahedron Lett.* **1975**, 3051-3054. (c) Hill, R. K.; Morgan, J. W. *J. Org. Chem.* **1968**, *33*, 927-928. (d) Sawada, S.; Oda, J.; Inouye, Y. *J. Org. Chem.* **1968**, *33*, 2141-2143. (e) Sawada, S.; Takehana, K.; Inouye, Y. *J. Org. Chem.* **1968**, *33*, 1767-1770.

(6) All yields refer to isolated and purified compounds. Satisfactory NMR and HRMS data were obtained for all compounds.

(7) Shank, R. S.; Shechter, H. *J. Org. Chem.* **1959**, *24*, 1825-1826.

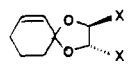
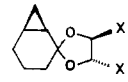
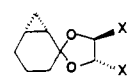
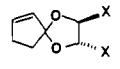
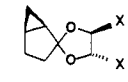
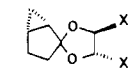
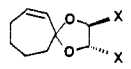
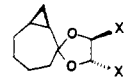
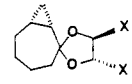
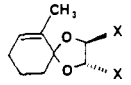
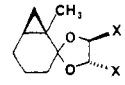
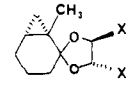
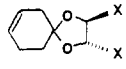
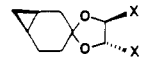
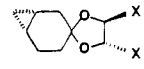
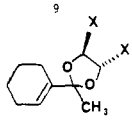
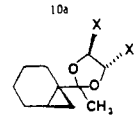
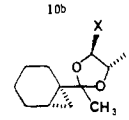
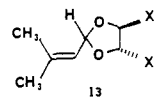
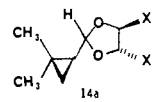
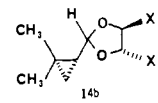
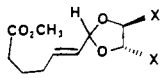
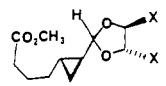
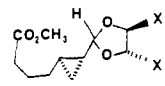
(8) Authentic diastereomeric mixtures of compounds **2**, **4**, **6**, **12**, and **16** were prepared for spectroscopic comparison by direct ketalization of the corresponding racemic cyclopropyl ketones with 1,4-di-*O*-benzyl-L-threitol. For previous examples of the use of ^{13}C NMR in determining diastereomer ratios, see: Hiemstra, H.; Wynberg, H. *Tetrahedron Lett.* **1977**, 2183-2186.

(9) Conditions for hydrolysis: 3% aqueous sulfuric acid, THF, room temperature, 3.5 h. Recovered (1*R*,6*S*)-bicyclo[4.1.0]heptan-2-one (83% yield) was spectroscopically and chromatographically identical with racemic material prepared by cyclopropanation of 2-cyclohexen-1-one (ref 4b, p 85). 1,4-Di-*O*-benzyl-L-threitol was also recovered. Similarly, hydrolysis of cyclopropane ketal **6** gave bicyclo[5.1.0]octan-2-one, $[\alpha]^{25}_D$ +25.7° (*c* 0.53, $CDCl_3$) in 75% yield, hydrolysis of **8** gave 1-methylbicyclo[4.1.0]heptan-2-one, $[\alpha]^{25}_D$ -19.4° (*c* 0.90, $CDCl_3$), in 81% yield, and hydrolysis of **12** gave 1-acetylbicyclo-[4.1.0]heptane, $[\alpha]^{26}_D$ -86.8° (*c* 0.37, $CDCl_3$), in 86% yield, the rotation of which corresponds to 93% optical purity (see ref 5a).

(10) The identities of the major diastereomers for the bicyclo[3.1.0]hexanone and bicyclo[5.1.0]octanone systems are assumed to be **4a** and **6a** in analogy with the observed preferential formation of **2a** from 2-cyclohexen-1-one ketal **1**. Work is currently in progress to confirm this assumption.

0002-7863/85/1507-8256$01.50/0

Table I. Diastereoselective Cyclopropanation of Homochiral Ene Ketals[a]

Entry	ene-ketal[b]	yield, %	$[\alpha]_D^{25}$, deg (α)[c]	product cyclopropane-ketals	yield, %	diastereomer ratio[d]
1	 1	93	+9.31 (4.18)	 2a  2b	90-98	9:1
2	 3	66	+0.23 (4.28)	 4a  4b	72	9:1
3	 5	82[e]	+1.69 (3.02)	 6a  6b	90	8:1
4	 7	63	+14.7 (1.92)	 8a  8b	99	20:1
5	 9	86	-9.66 (3.05)	 10a  10b	88	2:1
6	 11	75	-3.41 (3.23)	 12a  12b	88	14:1
7	 13	70	+8.85 (5.18)	 14a  14b	95	1:1
8	 15	48	+5.47 (3.80)	 16a  16b	62	1:1

[a] Reaction conditions: 400–700 mg of couple/mmol of ene ketal, 3 equiv of CH_2I_2, 0.5 M in refluxing diethyl ether, 1–4 h. [b] X = $CH_2OCH_2C_6H_5$. [c] In $CHCl_3$. [d] Determined by 62.9-MHz ^{13}C NMR spectroscopy. [e] Admixed with ≤10% of the isomeric 3-ene ketal and chromatographically separated prior to cyclopropanation.

(Table I). 2-Methyl-2-cyclohexen-1-one ketal **7** gave higher diastereoselectivity (20:1) than unsubstituted ketal **1**, while 3-cyclohexen-1-one ketal **9** gave much poorer diastereoselectivity (2:1). 1-Acetylcyclohexene ketal **11** gave high diastereoselectivity (14:1), while no diastereoselectivity was observed for acetals **13** and **15**.

Compounds **3**, **5**, **11**, **13**, and **15** were prepared[6] by direct ketalization of the corresponding α,β-unsaturated ketones and aldehydes using 1,4-di-*O*-benzyl-L-threitol as the diol component.[11] Compounds **1**, **7**, and **9** were prepared[6] by ketalization of 3-bromo-2-methoxycyclohexene, 2-bromo-2-methylcyclohexanone, and 4-tosyloxycyclohexanone, followed by elimination.[12] Yields appear in Table I.

The activating and directing effects of allylic and homoallylic oxygen atoms with regard to the Simmons–Smith reaction are well documented.[4,5,13] Chelation of zinc by oxygen can result in preferential delivery of the reagent to the closest of several double bonds and/or to a particular face of one double bond. This latter result is especially true for cycloalkenols. Note here that cyclic ketals **1**, **3**, **5**, **7**, **9**, and **11** exhibit diastereoselectivity, whereas acyclic acetals **13** and **15** exhibit little or no diastereoselectivity. The cyclic ketals could give more rigid zinc chelates than the acyclic acetals, resulting in more effective positioning of the Simmons–Smith reagent prior to methylene transfer. Ketal **9** exhibits substantially less diastereoselectivity than ketal **1**, presumably due to the increased distance of the double bond from the site(s) of zinc chelation. The greater diastereoselectivity observed for ketal **7** may be due to steric destabilization of one of several possible zinc chelate structures. Reasons for the remarkable diastereoselectivity observed for ketal **11** remain unclear. Work is currently under way to confirm and define the involvement of oxygen chelation in this diastereoselective cyclopropanation process.

Since cyclopropanes occur in a number of cyclic and acyclic natural products, and are also useful synthetic intermediates, the novel diastereoselective cyclopropanation described herein should prove a useful contribution to currently available but more cumbersome routes to such compounds.[5a,c,14]

Further uses of this and other homochiral protecting groups will be reported in future papers.[15]

(11) Ando, N.; Yamamoto, Y.; Oda, J.; Inouye, Y. *Synthesis* **1978**, 688–690.
(12) Garbisch, E. W., Jr. *J. Org. Chem.* **1965**, *30*, 2109–2120.
(13) Poulter, C. D.; Friedrich, E. C.; Winstein, S. *J. Am. Chem. Soc.* **1969**, *91*, 6892–6894.
(14) Johnson, C. R.; Schroeck, C. W. *J. Am. Chem. Soc.* **1968**, *90*, 6852–6854.
(15) Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Partial support of this research by Research Corporation and The American Cancer Society is gratefully acknowledged.

Registry No. 1, 99249-28-2; **2a**, 99249-29-3; **2b**, 99295-87-1; **3**, 99249-30-6; **4a**, 99249-31-7; **4b**, 99295-88-2; **5**, 99249-32-8; **5** (3-ene), 99249-33-9; **6a**, 99249-34-0; **6b**, 99295-89-3; **7**, 99249-35-1; **8a**, 99249-36-2; **8b**, 99295-90-6; **9**, 99249-37-3; **10a**, 99249-38-4; **10b**, 99295-91-7; **11**, 99249-39-5; **12a**, 99249-40-8; **12b**, 99295-92-8; **13**, 99249-41-9; **14a**, 99249-42-0; **14b**, 99249-43-1; **15**, 99249-44-2; **16a**, 99249-45-3; **16b**, 99295-93-9; $MeOC{=}CH(CH_2)_3CHBr$, 1728-36-5; $(PhCH_2OCH_2CHOH)_2$, 17401-06-8; $CH{=}CH(CH_2)_2CO$, 930-30-3; $CH{=}CH(CH_2)_3CO$, 1121-66-0; $MeBrC(CH_2)_4CO$, 10409-47-9; $TsOCH(CH_2)_2COCH_2CH_2$, 23511-04-8; $AcC{=}CHCH_2(CH_2)_2CH_2$, 932-66-1; $HOCH_2CH{=}CMeCH_3$, 556-82-1; $OHCCH{=}CMeCH_3$, 107-86-8; (*E*)-$HOCH_2CH{=}CH(CH_2)_3CO_2Me$, 76871-77-7; (*E*)-$HOCH_2CH{=}CH(CH_2)_3CHO$, 99249-48-6; 2-bromocyclohexane ketal, 99267-50-2; 2-bromo-2-methylcyclohexanone ketal, 99249-46-4; 4-tosylcyclohexanone ketal, 99249-47-

Supplementary Material Available: Experimental details for the preparation of compounds **1-16**, infrared, proton magnetic resonance, and mass spectral data for compounds **1-16**, and carbon magnetic resonance spectral data for compounds **2**, **4**, **6**, **8**, **10**, **12**, **14**, and **16** (15 pages). Ordering information is given on any current masthead page.

Pyrazolyl-Bridged Iridium Dimers. 10.[1] Sequential Addition at the Metal Centers in a Diiridium Configuration. Oxidatively Induced Relocation of a Bent, Terminal Nitrosyl Group To Occupy a Bridging Site

D. O. Kimberly Fjeldsted, Stephen R. Stobart,* and Michael J. Zaworotko

Department of Chemistry, University of Victoria British Columbia, Canada V8W 2Y2

Received August 7, 1985

Development of the chemistry of metal nitrosyl complexes has lagged behind that of the transition-metal carbonyl family despite certain obvious similarities between the character of nitrogen monoxide (nitric oxide, NO) and carbon monoxide as ligands.[2] The unique significance of CO as an accessible C_1 feedstock has provoked research into all aspects of its coordination behavior,[2] while the ambivalent electronic character of the NO ligand has worked against efforts to classify its properties.[3] Recently, however, interest in catalytic activation of NO (reductively[4] in combustion emissions, to N_2O or N_2, or C-N bond formation, via oximes[5] or to[6] diamines, or for[7] oxygen-transfer to organic substrates) has led to a more systematic search for parallels with existing steps in metal carbonyl chemistry. Thus migratory insertion[8,9] of coordinated NO and alkene[6] and alkyne[10] insertion into metal(μ-NO) bonds, as well as protonation and alkylation of terminal[11] and μ_3-bridging[12] NO groups, are now established. We describe two-center oxidative-addition to a cationic diiridium(II) complex as a result of which a bent, terminal NO group takes up a bridging position. Such a process has not been reported previously, although the analogous transformation involving CO is well-known[2] and like isoelectronic carbonyl complexes $[Cr(\eta\text{-}C_5H_5)(NO)_2]_2$ is subject to intramolecular terminal/bridge ligand site exchange.[13]

Addition to a solution in CH_2Cl_2 of the purple-red diiridium(I) complex $[Ir(COD)(\mu\text{-}pz)]_2$ (**1**, COD = cycloocta-1,5-diene; pzH = pyrazole) of $NOBF_4$ resulted in immediate darkening of the reaction mixture. Stirring (1 h) then filtration, precipitation with Et_2O and finally recrystallization from CH_2Cl_2/Et_2O afforded lustrous, purple-black crystals of a product (**2**) which was deduced to be a cationic diiridium nitrosyl complex on the basis of IR, NMR (Table I), and analytical data.[14] The geometry of the cation, which was determined using single-crystal X-ray diffraction,[15] is shown in Figure 1. Treatment of compound **2** with

Table I. IR[a] and ^1H NMR[b] Data

compd	ν_{NO}/cm^{-1}	^1H NMR/ppm
2	1680	7.67 d[c] (2), 7.57 d[c] (2), 6.49 t[d] (2)
3	1700[e]	7.71 d[c] (2), 7.50 d[c] (2), 6.50 t[d] (2)
4a	1630	7.75 d[c] (4), 6.40 t[d] (2)

[a] KBr pellet. [b] Recorded at 250.0 MHz, Bruker WM250 Spectrometer, CD_2Cl_2 solution; relative intensities are given in parentheses. [c] H^3/H^5 of μ-pz. [d] H^4 of μ-pz. [e] ν_{CO} at 2065 cm^{-1}.

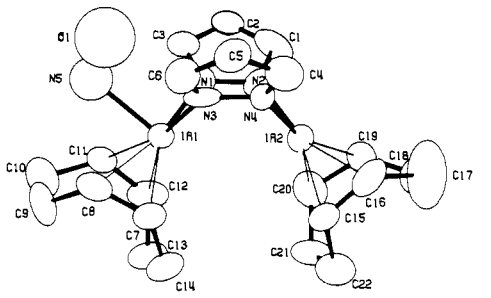


Figure 1. ORTEP drawing of the cation in complex **2**. Selected bond distances and angles: Ir(1)-Ir(2), 3.224 (1); Ir(1)-N(1), 2.021 (19); Ir(1)-N(3), 2.051 (19); Ir(1)-N(5), 2.081 (33); N(5)-O(1), 1.012 (50); Ir(2)-N(2), 2.041 (21); Ir(2)-N(4), 2.077 (17); Ir(1)-C(7), 2.209 (25); Ir(1)-C(8), 2.262 (24); Ir(1)-C(11), 2.255 (25); Ir(1)-C(12), 2.211 (24); Ir(2)-C(15), 2.143 (24); Ir(2)-C(16), 2.166 (27); Ir(2)-C(19), 2.173 (24); Ir(2)-C(20), 2.122 (28) Å. N(1)-Ir(1)-N(3), 89.4 (8)°; N(2)-Ir(2)-N(4), 87.9 (7)°; Ir(1)-N(5)O(1), 111.3 (41)°. Unresolved disorder or high thermal motion results in the uncertainties in the positions of N(5) and O(1); See also: Mingos, D. M. P.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 1035. Mingos, D. M. P.; Robinson, W. T.; Ibers, J. A. *Ibid.* **1971**, *10*, 1043.

(1) Part 9. Fjeldsted, D. O. K.; Stobart, S. R. *J Chem. Soc., Chem. Commun.* **1985**, 908.

(2) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980. Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980.

(3) (a) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339. (b) Raynor, J. B. *Inorg. Chim. Acta* **1972**, *6*, 347.

(4) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53. Pandey, K. K. *Coord. Chem. Rev.* **1983**, *51*, 69.

(5) Seidler, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 110.

(6) Becker, P. N.; White, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5676.

(7) Tovrog, B. S.; Diamond, S. E.; Mares, F.; Szalkiewicz, A. *J. Am. Chem. Soc.* **1981**, *103*, 3522. Andrews, M. A.; Cheng, C. W. F. *J. Am Chem. Soc.* **1982**, *104*, 4268. Tovrog, B. S.; Mares, F.; Diamond, S. E. *J. Am. Chem. Soc.* **1980**, *102*, 6618.

(8) Weiner, W. P.; White, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3612. Weiner, W. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3922.

(9) Seidler, M. D.; Bergman, R. G. *Organometallics* **1983**, *2*, 1897.

(10) Clamp, S.; Connelly, N. G.; Howard, J. A. K.; Manners, I.; Payne, J. D. *J. Chem. Soc., Dalton Trans.* **1984**, 1659.

(11) (a) Grundy, K. R.; Reed, C. A.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1970**, 1501. (b) Wilson, R. D.; Ibers, J. A. *Inorg. Chem.* **1979**, *18*, 336.

(12) (a) Stevens, R. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1982**, *104*, 6454. (b) Legzdins, P.; Nurse, C. R.; Rettig, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3727.

(13) Kirchner, R. M.; Marks, T. J.; Kristoff, J. S.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 6602.

(14) Compound **2**. Anal. Calcd for $C_{22}H_{30}BF_4Ir_2N_5O$: C, 31.02; H, 3.55; N, 8.22. Found: C, 30.95; H, 3.31; N, 8.01. Compound **3**. Anal. Calcd for $C_{23}H_{30}BF_4Ir_2N_5O_2$: C, 31.40; H, 3.44; N, 7.96. Found: C, 31.32; H, 3.40; N, 8.53. Compound **4a**. Anal. Calcd for $C_{22}H_{30}BCl_2F_4Ir_2N_5O$: C, 28.64; H, 3.28; N, 7.59. Found: C, 28.31; H, 3.67; N, 7.40. Compound **4b**. Anal. Calcd for $C_{22}H_{30}BF_4I_2Ir_2N_5O$: C, 23.90; H, 2.74; N, 6.33. Found: C, 24.25; H, 2.79; N, 5.85.

(15) Crystal data for compound **2**: M_r 851.7; monoclinic; space group $P2_1/n$; a = 14.645 (5) Å, b = 13.446 (4) Å, c = 13.391 (2) Å; β = 112.24 (2)°; V = 2441 Å^3; Z = 4; D_{calcd} = 2.32 g cm^{-3}; Picker four circle diffractometer, Mo Kα (λ = 0.71069 Å) radiation, μ = 105.4 cm^{-1}; 2852 observed reflections refined to a conventional R = 0.070 (R_w = 0.071).

0002-7863/85/1507-8258$01.50/0