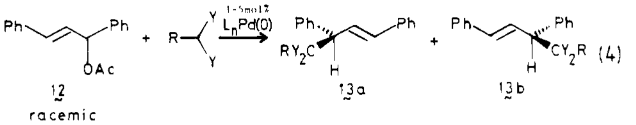
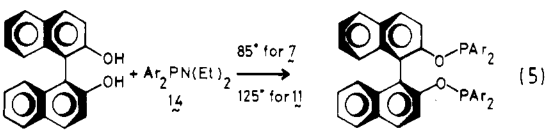
Allyl acetate 12 also undergoes alkylation using 6 or 7 as the optically active ligands as summarized in eq 4. Phase-transfer conditions were required for the bis(benzenesulfonyl)methane system since no alkylation occurred with BSA in THF. Strikingly, only a small effect of either temperature or steric demand of the nucleophile is observable as delineated in eq 4. The absolute configuration of 13a, assigned by degradation to dimethyl (+)-S-2-phenylsuccinate[10] can also be rationalized by a model similar to that depicted in Figure 2. The reversal of the sense of induction of 13 with BINAP is potentially due to syn–anti interconversion (which is not possible with lactone 8).



L	R	Y	condtns	% 13a	% 13b	% ee	% yield
6	CH_3	CO_2Me	BSA, THF, 66 °C	25	75	50	81
7	H	CO_2Me	BSA, THF, 66 °C	78	22	55	87
7	CH_3	CO_2Me	BSA, THF, 25 °C	84	16	68	75
7	H	SO_2Ph	$(n\text{-Bu})_4NOH$, 25 °C CH_2Cl_2, H_2O	83	17	66	85

The high asymmetric induction for C–C bond formation ultimately possible in all the reactions reported herein demonstrates that diastereomeric complexes need not be the source of asymmetric induction in metal-catalyzed allylic alkylations. An electronic effect as observed in enantiomerically pure stoichiometric molybdenum complexes[11] appears unlikely as the source of the asymmetric induction. The observation of good ee in spite of the unfavorable orientation of the incoming nucleophile with respect to the centers of asymmetry supports the notion that these ligands begin to create chiral pockets. The practical operating temperature of these alkylations combined with the ready availability of the chiral ligands from the commercially available, optically active 1,1′-binaphthol[12] according to eq 5[12] enhances the utility of this approach. It is interesting to note that the *more flexible* ligand 7 provides higher induction than the more rigid ligand 6 in contrast to other asymmetric catalytic reactions such as hydrogenation.[13]



Acknowledgment. We wish to thank the National Science Foundation for their generous support of our programs. We thank Johnson Matthey and Englehardt for generous supplies of palladium salts and Dr. Larry Truesdale and Hoffmann La Roche Inc. for a generous gift of optically pure BINAP.

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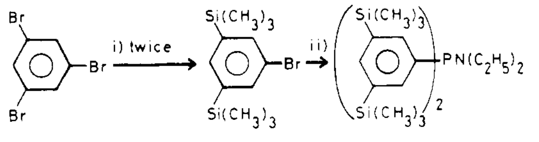
(9) The synthesis of the requisite 14 (Ar = 3,5-bis(trimethylsilyl)phenyl) proceeds simply from 1,3,5-tribromobenzene as depicted.



(i) n-C_4H_9Li, ether, −78 °C, then Me_3SiCl; (ii) n-C_4H_9Li, THF, −78 °C; then 0.4 equiv of Cl_2PNEt_2, −78 °C–room temperature

(10) Petterson, K. *Ark. Kem.* **1954**, *7*, 39, 347.

(11) Faller, J. W.; Chao, K.-H. *J. Am. Chem. Soc.* **1983**, *105*, 3893; *Organometallics* **1984**, *3*, 927.

(12) Available from Aldrich Chemical Co. or by direct oxidative coupling of β-naphthol in the presence of *d*-amphetamine. See: Brussee, J.; Jansen, A. C. A. *Tetrahedron Lett.* **1983**, *24*, 3261. In our hands, more forcing conditions (toluene, 85 °C) were required than those reported by: Grubbs, R. H.; DeVries, R. A. *Tetrahedron Lett.* **1977**, 1879.

(13) It should be noted that less than 3 equiv of chiral ligand 11/Pd led to substantially lower % ee. The significance of this important observation with respect to the exact structure of the active catalyst is not known. In other cases, we have observed variation of ee with the ratio of phosphine to palladium. In these cases, the conditions which give the highest ee are reported.

Ancillary Ligand Involvement in the Activation of Dihydrogen by Iridium(III) Complexes

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Received October 18, 1984

Summary: Oxidative addition of methyl iodide to the Ir(I) complexes $Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PR_2)_2]$ (R = Ph, *i*-Pr) yields monomeric, five-coordinate methyl iodide derivatives $Ir(CH_3)I[N(SiMe_2CH_2PR_2)_2]$. Spectroscopic and crystallographic data indicate that these species are square pyramidal with the methyl ligand in the apical position. The complex $Ir(CH_3)I[N(SiMe_2CH_2P(i\text{-}Pr)_2)_2]$ is monoclinic, crystallizing in the $P2_1/m$ space group with a = 9.6295 (7) Å, b = 15.2327 (5) Å, c = 10.4068 (9) Å, α = 90°, β = 111.774 (4)°, γ = 90°, Z = 2, and R_w = 0.029. Under dihydrogen, these complexes rapidly form the Ir(III) amine hydrides $Ir(CH_3)I(H)[NH(SiMe_2CH_2PR_2)_2]$ having a stereochemistry which corresponds to an overall trans addition of H_2. Unit cell parameters for $Ir(CH_3)I(H)[NH(SiMe_2CH_2P(i\text{-}Pr)_2)_2]$, which is triclinic and belongs to the $P\bar{1}$ space group, are as follows: a = 11.412 (2) Å, b = 14.712 (3) Å, c = 9.9133 (13) Å, α = 106.972 (9)°, β = 112.406 (8)°, γ = 70.989 (13)°, Z = 2, and R_w = 0.040. Crystallographic data for both of these complexes were collected at 22 °C by using an Enraf-Nonius CAD4-F diffractometer with Mo Kα radiation. It would appear that H_2 activation by these iridium complexes occurs via an oxidative addition/reductive transfer pathway rather than a direct heterolytic cleavage of H_2.

The activation of dihydrogen by transition-metal complexes can occur via oxidative addition, homolysis, or heterolysis depending upon the nature of the metal center, its oxidation state, coordinated ligands, and the solvent basicity.[1] Although heterolytic cleavage is purported to occur for a number of Rh(III)[2,3] and Ir(III)[4] species under H_2, the evidence for this mechanism vs. an oxidative ad-

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[†] Fellow of the Alfred P. Sloan Foundation (1984–1986).

(1) Brothers, J. P. *Prog. Inorg. Chem.* **1981**, *28*, 1.

(2) Halpern, J.; Harrod, J. F. *Can. J. Chem.* **1959**, *37*, 1933.

(3) James, B. R.; Rempel, G. L. *Can. J. Chem.* **1966**, *44*, 233.

(4) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973; p 313.

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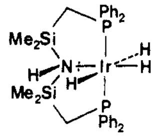
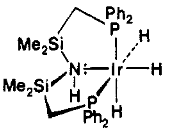
dition/reductive elimination pathway is scant.

In a previous communication,[5] we reported the stereoselective oxidative addition behavior of a series of iridium(I) amides with dihydrogen. Of particular interest was the observation that $Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PPh_2)_2]$ under excess H_2 generated an iridium(III) amine trihydride, 1. Although the mechanism of its formation has not been fully elaborated, production of 1 formally corresponds to a ligand-assisted heterolysis of dihydrogen. Structural characterization of 1 was established through standard spectroscopic methods only, since its inherent instability toward loss of dihydrogen precluded solid-state analysis. The corresponding facial isomer 2, although moderately stable, could not be obtained as suitable crystals for an X-ray crystallographic determination. However, we have been able to find corroborating evidence for these structural formulations in some related chemistry of a series of Ir(III) alkyl halides.

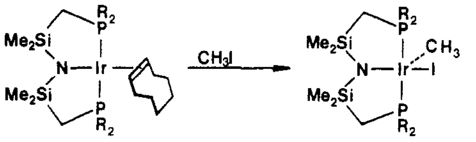


1



2

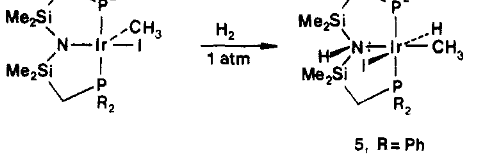
Oxidative addition of methyl iodide to $Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PR_2)_2]$ (R = Ph, *i*-Pr) proceeds smoothly at room temperature in either toluene or hexanes to generate essentially quantitative yields of deep green, monomeric Ir(III) methyl iodide derivatives 3 and 4 (eq 1). Both complexes are believed to have a distorted square-pyramidal stereochemistry with the methyl group in the apical position; this structural assignment was based on a combination of ^1H NMR data[6,7] and an X-ray crystal structure of 4.[8]



(1)

3, R=Ph
4, R=i-Pr

The chemistry of these complexes with dihydrogen is quite spectacular. Under 1 atm of H_2 at room temperature in toluene or hexanes, deep green solutions of 3 or 4 decolorize within minutes. Solvent removal followed by crystallization from hexanes yields colorless crystals of 5 and 6 (eq 2) as the major products (>75% yields). Once again, both spectroscopic[9,10] and crystallographic information were required for full structural elucidation. As illustrated by the solid-state structure of 6 (Figure 1), protonation of the amide center has occurred and the hydride, although not refined, was also located.



(2)

5, R=Ph
6, R=i-Pr

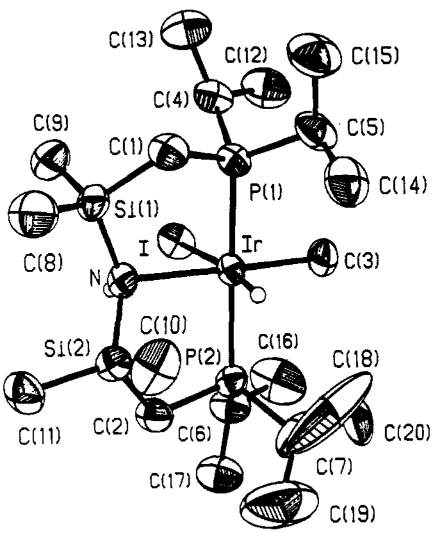
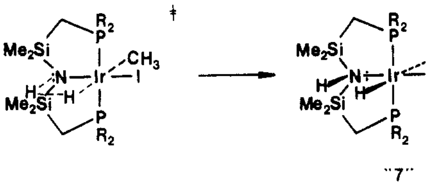


Figure 1. Perspective view of $Ir(CH_3)I(H)[NH(SiMe_2CH_2P(i\text{-}Pr)_2)_2]$. Important bond lengths (Å) are as follows: Ir–I, 2.8176 (4); Ir–P(1), 2.3070 (13); Ir–P(2), 2.3152 (14); Ir–N, 2.368 (4); Ir–C(3), 2.127 (6); Ir–H(Ir), 1.65; N–H(N), 0.70 (8).

Although 5 and 6 can be viewed as the result of a heterolytic activation of dihydrogen, it is not clear at this point whether this term accurately describes their mode of formation. On one hand, the alkyl halide complexes 3 and 4 would appear to be ideal candidates for heterolysis, since they contain metals in a high oxidation state coordinated to a ligand containing a basic site (amide) capable of accepting a proton. However, the crystal structure of 6 would tend to discredit this possibility, since a concerted ionic splitting of H_2 should lead to a species of structure "7", containing a trans methyl/hydride grouping and having the N–H bond cis to the Ir–H unit (eq 3).



(3)

"7"

Alternatively, oxidative addition of H_2 to form an Ir(V) dihydride, followed by rearrangement of this seven-coordinate intermediate, and reductive transfer[11] could explain the observed configuration.[12] Although neither mecha-

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(5) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 682.

(6) **3**: ^1H NMR (δ, C_6D_6) $SiCH_3$, –0.13 (s), 0.44 (s), CH_2P, 1.64 (t, J_{app} = 4.6 Hz), $IrCH_3$, 2.02 (t, $J_{H,P}$ = 6.0 Hz), $P(C_6H_5)_2$, 7.13 (m, para/meta), 7.80 (m, ortho). Anal. Calcd for $C_{31}H_{39}IIrNP_2Si_2$: C, 43.15; H, 4.56; N, 1.62. Found: C, 43.28; H, 4.64; N, 1.69.

(7) **4**: ^1H NMR (δ, C_6D_6) $SiCH_3$, 0.42 (s), 0.43 (s), CH_2P, 0.85 (t, J_{app} = 5.2 Hz), $IrCH_3$, 2.42 (t, $J_{H,P}$ = 4.8 Hz), $P\{CH(CH_3)_2\}_2$, 1.10 (m), $P\{CH(CH_3)_2\}_2$, 2.77 (m). Anal. Calcd for $C_{19}H_{47}IIrNP_2Si_2$: C, 31.40; H, 6.52; N, 1.93. Found: C, 31.70; H, 6.50; N, 1.92.

(8) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J., manuscript in preparation.

(9) **5**: ^1H NMR (δ, C_6D_6) $SiCH_3$, 0.04 (s), 0.42 (s), $IrCH_3$, 1.28 (t, $J_{H,P}$ = 6.2 Hz), CH_2P, 1.75 (dt, J_{app} = 4.2 Hz, J_{gem} = 12.5 Hz), 2.16 (dt, J_{app} = 6.0 Hz), $P(C_6H_5)_2$, 7.17 (m, para/meta), 7.63, 7.87 (m, ortho); IrH, –19.50 (t, $J_{H,P}$ = 13.7 Hz); IR (cm^{-1}, C_6D_6) ν_{IrH} 2200 (br, m), ν_{NH} 3135 (w). Anal. Calcd for $C_{31}H_{41}IIrNP_2Si_2$: C, 43.05; H, 4.78; N, 1.62. Found: C, 42.70; H, 4.60; N, 1.60.

(10) **6**: ^1H NMR (δ, C_6D_6) $SiCH_3$, 0.11 (s), 0.29 (s), CH_2P, 1.15 (m), $IrCH_3$, 1.15 (m), $P\{CH(CH_3)_2\}_2$, 1.15 (m), 1.49 (m), $P\{CH(CH_3)_2\}_2$, 2.18 (m), 3.39 (m), IrH, –21.41 (t, $J_{H,P}$ = 14.5 Hz); IR (cm^{-1}, KBr) ν_{IrH} 2235 (m), ν_{NH} 3180 (w). Anal. Calcd for $C_{19}H_{49}IIrNP_2Si_2$: C, 31.31; H, 6.78; N, 1.92. Found: C, 31.60; H, 6.86; N, 1.88.

(11) The term reductive *transfer* is more accurate than reductive *elimination* since the amine ligand is retained in the coordination sphere.

(12) An interesting comparison can be noted in the reactivity of an iridium carbene complex with dihydrogen,[13] for which the product's stereochemistry also corresponds to an overall trans addition of H_2. However, it is difficult to envision a common mechanism for its formation with that of **5** and **6**.

(13) Crocker, C.; Empsall, H. D.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1217.

nism can be ruled out, it would appear that the heterolytic pathway is less likely based on the available evidence. Whichever process is operative, it would seem reasonable to assume that the Ir(III) amine trihydrides 1 and 2 are formed in a similar fashion. Further investigation into these reactions as well as the chemistry of the rhodium analogues is underway.

Acknowledgment. Financial support was provided by NSERC of Canada and the Alfred P. Sloan Foundation. We gratefully thank Johnson-Matthey for the loan of $IrCl_3$. We also thank Professor James Trotter for the use of his X-ray diffractometer and structure solving programs.

Registry No. **3**, 96110-11-1; **4**, 96110-12-2; **5**, 96110-13-3; **6**, 96110-14-4; $Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PPh_2)_2]$, 84074-30-6; $Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2P(i\text{-}Pr)_2)_2]$, 96110-15-5; H2, 1333-74-0.

Supplementary Material Available: Tables containing crystallographic data, bond lengths, bond angles, intraannular torsion angles, final positional and isotropic thermal parameters, and structure factor amplitudes (70 pages). Ordering information is given on any current masthead page.

Additions and Corrections

Arnold L. Rheingold* and Mark E. Fountain: Coordinated Homoatomic Polyorganophosphorus Catenates. The Crystal Structure and Molecular Geometry of $Fe_2(CO)_6(PCH_3)_4$ and $Fe_2(CO)_6(PC_6H_5)_4$. **1984**, *3*, 1417.

Page 1420, Table V: the "butterfly" dihedral angle for compound IV is 112.3 (2)° and for V is 105.0 (1)°.

Hubert Le Bozec, Pierre H. Dixneuf,* and Richard D. Adams: Stabilization of a Metal–Carbene Intermediate by Formation of a Metal–Mercury(II) Bond. Synthesis and X-ray Structure of $Cl_2HgFe(=\overline{CSC(CO_2Me)=C(CO_2Me)S})(CO)_2(PMe_2Ph)_2$. **1984**, *3*, 1919.

In the printed version of this communication, the title was left out.

Book Reviews

A Pictorial Approach to Molecular Structure and Reactivity. By R. F. Hout, Jr., W. J. Pietro, and W. J. Hehre. Wiley, New York. 1984. $39.94. 403 + xi pages.

This book contains about 1500 photographs of the STO-3G or STO-3G* molecular orbitals of 120 molecules or complexes and four transition structures. A brief accompanying text describes some basic ideas about molecular orbitals and bonding, along with qualitative descriptions of some of the more interesting aspects of the photographs. All valence MOs plus the LUMO are shown for each entity which is included. Of particular interest to readers of this journal, the MOs of various inorganic and organometallics are shown, including several compounds containing Ag, Fe, Ti, Cr, and Mo, ranging from the simple (e.g., AgCl and H_2CTiH_2) to the complex (e.g., $Fe(CO)_5$ and bis(benzene)chromium), along with simple organolithium compounds up to methyllithium tetramer. This book invites comparison to the classic in this area, Jorgensen and Salem's "The Organic Chemists' Book of Orbitals", published in 1973. Jorgensen and Salem has a more extensive introduction to MO and perturbation theory and plots of orbitals of many organic molecules. The Jorgensen 3D contour plots have become the "industry standard" for MO display. Hehre et al. have devised extraordinarily beautiful high-resolution color graphic displays of orbitals, but only black and white photographs are presented in this book, presumably to keep the price of the book relatively modest. The black and white photographs sometimes have insufficient contrast to show some details. Nevertheless, the book does include the MOs of a variety of organometallics and inorganic molecules and should provide a useful adjunct text for courses on organic and inorganic bonding.

K. N. Houk, *University of Pittsburgh*

Allenes in Organic Synthesis. By H. F. Schuster and G. M. Coppola. Wiley, New York. 1984. XVI + 358 pages. $47.50.

Allenes and cumulenes in general have intrigued chemists ever since their discovery in the last century. In the intervening years their chemistry has evolved to the point where allenes have been discovered in diverse natural products and employed in complex syntheses. This monograph deals with the preparation of allenes and their uses in organic synthesis.

Chapter one provides a short historical introduction and a brief description of the structural, spectral, and optical properties of allenes. Chapter two treats the preparation of terminal, internal, and cyclic allenes. Chapter three discusses hydrogenation of and electrophilic, nucleophilic, and miscellaneous additions to allenes. Chapter four covers allenes with unsaturated substituents, such as vinyl and acetylenic allenes, and their uses. Chapter five deals