$Ni_2(\mu\text{-}OH)(\mu\text{-}OAc)_2(TACN)^+$.[13]

In acetonitrile **1** displays three broad absorption bands at 373 ($\epsilon = 60.0\ M^{-1}\ cm^{-1}$), 622 ($\epsilon = 20.4\ M^{-1}\ cm^{-1}$), and 1037 nm ($\epsilon = 25.4\ M^{-1}\ cm^{-1}$). These peaks are assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3T_{1g}(F)$, and $^3T_{2g}(F)$ transitions expected for octahedral d^8 ions.[16] A weak absorption also is observed at 767 nm due to the spin forbidden $^3A_{2g} \rightarrow {}^1E_{1g}$ transition. Evaluation of the data with a d^8 energy level diagram[17] gives $D_q = 970\ cm^{-1}$ and $B \simeq 940\ cm^{-1}$. Urease also displays three prominent bands in the visible and near-IR region at 407, 745, and 1060 nm.[5] Addition of excess ammonium carbamate to an aqueous solution of **1** results in the formation of a bridged carbamate complex[18] which displays clean isobestic behavior and absorption peaks at 370 ($\epsilon = 220.0\ M^{-1}\ cm^{-1}$), 615 ($\epsilon = 26.0\ M^{-1}\ cm^{-1}$), 768 ($\epsilon = 6.0\ M^{-1}\ cm^{-1}$) and 1015 ($\epsilon = 25.0\ M^{-1}\ cm^{-1}$). The reactivity of the carbamate complex toward strong base as well as **1** with urea and other known substrates of urease are under investigation.

The electrochemical properties of **1** have been studied by cyclic voltammetry. A single quasireversible one-electron[20] redox wave is observed in acetonitrile at +0.94 V vs Ag/AgCl corresponding to the $Ni^{II}Ni^{II}/Ni^{II}Ni^{III}$ couple. Similar electrochemical behavior has been reported for the $[Ni_2(\mu\text{-}OH)(\mu\text{-}OAc)_2(TACN)]$[13] ion and related Ni^{II} complexes.[21] Efforts to isolate the mixed-valence $[Ni^{II}Ni^{III}\ (bimp)\ (\mu\text{-}OAc)_2]^{2+}$ complex are in progress.

The solid-state variable-temperature magnetic susceptibility of **1** has been measured between 300.9 and 5.5 K. The effective magnetic moment of the cation changes gradually from 4.69 μ_B/complex at 300.9 K to 2.88 μ_B/complex at 5.5 K[22] suggesting the presence of a weak antiferromagnetic exchange interaction. The data were least-squares (25 × 25) fit by a full-matrix diagonalization approach which includes both an isotropic exchange interaction ($H = -2J\hat{S}_1\cdot\hat{S}_2$) as well as single-ion zero-field splitting (DS_z^2 where D is the axial zero-field-splitting parameter) for each Ni(II) ion to give $g = 2.2$, $D = -0.02\ cm^{-1}$, and $J = -1.9\ cm^{-1}$. The weak exchange interaction is consistent with the magnetic data discussed earlier for urease.[8]

Acknowledgment. We are thankful for support from the National Science Foundation (Grant RII-8610671) and the Commonwealth of Kentucky through the Kentucky EPSCoR Program (R.M.B.) and National Institutes of Health Grant HL13652 (D.N.H.). Dr. C. Trapp's contribution in determining ligand field parameters for **1** are acknowledged.

Supplementary Material Available: Tables containing atomic positional parameters, isotropic and anisotropic thermal parameters, selected bond lengths and angles, and magnetic data and figures of electrochemical and electronic spectral properties for $[Ni_2(bimp)(\mu\text{-}OAc)_2]ClO_4\cdot CH_3OH$ (**1**) are available (12 pages); table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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[18] The same di-μ-carbamate complex can be prepared by reaction of 2 equiv of nickel(II) perchlorate and ammonium carbamate with bimp in a methanol solution. The compound analyzes correctly for the formula $[Ni_2(bimp)(\mu\text{-}O_2CNH_2)_2]\cdot ClO_4\cdot CH_3OH$.

[19] Inhibitors such as phosphoramidates and dihydrogen phosphate monoanion also are thought to bridge the nickel ions in urease, requiring the Ni–Ni separation to be less than 6 Å, further supporting the proposal of a binuclear active site.

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[22] Compound **1** also displays an X-band EPR spectrum at 4.2 K (with features at $g = 6.67, 4.17, 2.24$ and 2.17) for both a microcrystalline-powdered sample and frozen acetonitrile solution of the complex.

Thermal and Photochemical Rearrangements of Methyliridium Phosphido Complexes: Formation of a Cyclometalated Hydride by α-Abstraction of a Coordinated Alkyl Ligand

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One of the fundamental reactions of mononuclear hydrocarbyl metal complexes is the α-elimination or α-abstraction process.[1] Although this process is quite well-documented[2] for the earlier transition metals, recent studies[3] have suggested that complexes of the later metals are also amenable to this process. In particular, we have previously reported the photochemical generation of an iridium methylidene[4] and the unusual mode of dihydrogen activation by a terminal phosphide complex,[5] both processes apparently involving elimination or transfer of an α-hydrogen from a coordinated hydrocarbyl group. In this paper we provide yet another example of this type of reaction in the *thermal* rearrangement of iridium(III) methyl complexes containing terminal phosphide ligands. Also presented is the contrasting apparent coupling of an alkyl and a terminal phosphide ligand under *photochemical* conditions to give a coordinated phosphine.

The iridium(III) diphenylphosphido complex[5] $Ir(CH_3)PPh_2[N(SiMe_2CH_2PPh_2)_2]$, **1a**, is thermally unstable; at 50 °C in the dark, deep purple solutions of **1a** slowly (5 h) fade to light yellow to generate the octahedral hydride complex[6] *fac*-$Ir(\eta^2\text{-}CH_2PPh_2)H[N(SiMe_2CH_2PPh_2)_2]$, **2a**, in high yield. The X-ray crystal structure[7] of **2a** is shown in Figure 1 along with some pertinent bond parameters. The ancillary tridentate ligand has isomerized to the facial coordination mode with the hydride trans to the amide donor; the η^2-CH_2PPh_2 moiety occupies the remaining cis sites of the distorted octahedron. Although **2a** is stable in the solid state under an inert atmosphere, further heating in solution results in the *irreversible* formation of the iridium(I) complex $Ir(PMePh_2)[N(SiMe_2CH_2PPh_2)_2]$, **3a**. Photolysis[8] of the Ir(III) phosphide complex **1a** at room temperature results in the direct formation of the Ir(I) complex **3a** with no evidence for the intermediacy of the cyclometalated hydride complex **2a**. These

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[6] Analytical and NMR data are contained in the Supplementary Material.

[7] Crystals of *fac*-$Ir(\eta^2\text{-}CH_2PPh_2)H[N(SiMe_2CH_2PPh_2)_2]$ (**2a**) are monclinic having the cell constants 9.253 (2) Å, 21.950 (5) Å, 20.081 (4) Å, and 90.74 (2)°; other crystal data are $Z = 4$ and space group $P2_1/c$. The structure was solved by conventional heavy-atom techniques and was refined in blocks (with the Ir atom in every cycle) using least-squares procedures to $R = 0.0356$ and $R_w = 0.0370$ for 4448 reflections having $I > 3\sigma(I)$ collected at 20 ± 1° with Mo Kα radiation on a Nicolet R3 diffractometer. All the atoms were refined anisotropically except for the hydrogen atom on iridium which was refined isotropically; all other hydrogens were fixed in idealized positions. Full details will be reported elsewhere.

[8] The photolysis of **1a** was carried out using a 275 W sunlamp for 24 h at room temperature; however, photolysis of the more thermally labile complex **1b** required use of a N_2 laser with the sample maintained at −30 °C.

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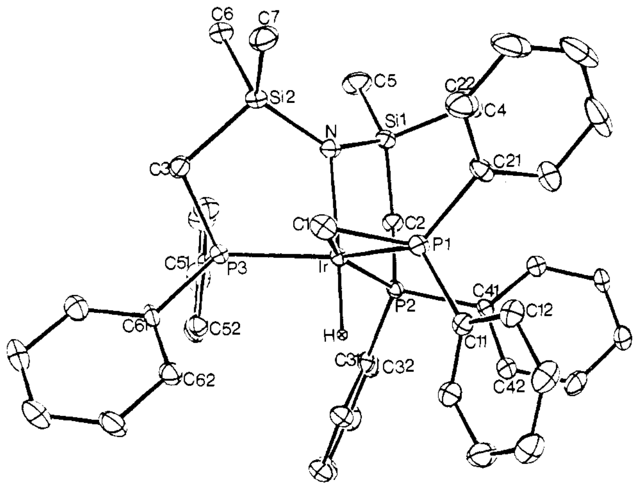
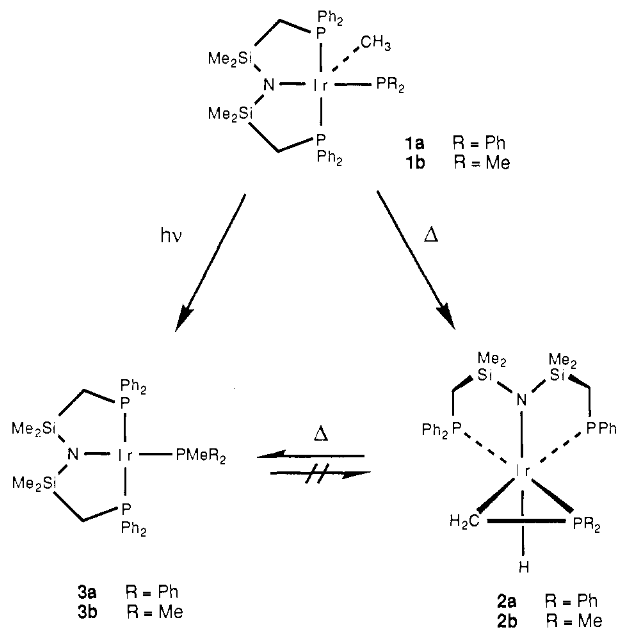


Figure 1. ORTEP drawing of $Ir(\eta^2\text{-}CH_2PPh_2)H[N(SiMe_2CH_2PPh_2)_2]$ (**2a**) showing thermal ellipsoids at the 20% probability level. Hydrogen atoms are drawn arbitrarily small. Atoms with numbers only are carbon atoms. Selected bond lengths (Å) and angles (deg) are as follows: Ir–N, 2.277 (6); Ir–H, 1.51 (6); Ir–C(1), 2.203 (7); Ir–P(1), 2.241 (2); Ir–P(2), 2.272 (2); Ir–P(3), 2.291 (2); P(1)–Ir–P(2), 110.9 (1); P(1)–Ir–P(3), 144.5 (1); P(2)–Ir–P(3), 104.5 (1); P(1)–Ir–C(1), 46.7 (2); Ir–P(1)–C(1), 65.5 (2); N–Ir–C(1), 97.6 (3).

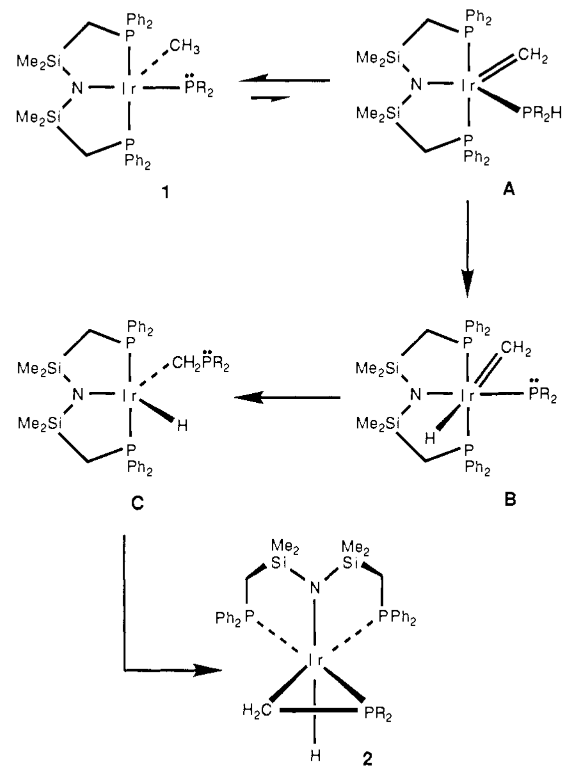
Scheme I



results taken together (Scheme I) argue for a thermal rearrangement of the starting phosphide which does *not* involve prior reductive elimination to the iridium(I) phosphine complex followed by intramolecular cyclometalation of the coordinated $PMePh_2$ group. Rather, the cyclometalated hydride **2a** is the kinetic product in the thermolysis of **1a**. The analogous dimethylphosphido complex[6] $Ir(CH_3)PMe_2[N(SiMe_2CH_2PPh_2)_2]$, **1b**, which is formed by reaction of $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ with $KPMe_2$ at -30 °C, also rearranges thermally (above -20 °C) to the cyclometalated hydride derivative[6] *fac*-$Ir(\eta^2\text{-}CH_2PMe_2)H[N(SiMe_2CH_2PPh_2)_2]$ (**2b**). Further heating of **2b** at 50 °C for extended periods generates the Ir(I) complex $Ir(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$, **3b**. Furthermore, the same trimethylphosphine complex **3b** is the observed product when **1b** is photolyzed at -30 °C for 3 h (Scheme I).

To account for the formation of the kinetic products **2**, it is proposed (Scheme II) that the methyl group of **1** undergoes a reversible α-abstraction by the phosphide[5] to generate a methylidene phosphine species A which subsequently oxidatively adds the phosphine P–H bond to form the hydride phosphide species B; migratory insertion of the methylidene to the phosphide generates a transient hydrido-η^1-methylenephosphine complex C. The lone pair on the uncoordinated phosphine of C can then bind to the coordinatively unsaturated Ir(III) center to generate the observed complex **2**. Other mechanistic proposals can be invoked. For example, rather than α-abstraction by the phosphide ligand, α-elimination directly to the iridium also provides a route to the hydrido-η^1-methylenephosphine complex C (after migratory insertion of the methylidene) and is consistent with the limited mechanistic data obtained so far.

Scheme II



The observation of the $L_nM(\eta^2\text{-}CH_2PR_2)H$ moiety by rearrangement of a methyl phosphido complex $L_nM(CH_3)PR_2$ is unprecedented. However, cyclometalation of coordinated phosphines does lead[9] to complexes with the $\eta^2\text{-}CH_2PR_2$ unit, although, as discussed above, this certainly is not occurring in our systems. Another procedure involves metathesis[10] with lithiated phosphines such as $LiCH_2PR_2$ or $LiC(SiMe_3)_2PMe_2$. Interestingly, the reaction of $LiCH_2PPh_2\cdot TMEDA$ with $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ leads to the analogous complex $Ir(CH_3)(\eta^2\text{-}CH_2PPh_2)[N(SiMe_2CH_2PPh_2)_2]$, which also has the *facial* geometry for the ancillary tridentate ligand, thus providing precedent for the conversion of the proposed intermediate C to **2** as shown in Scheme II.

The results described here are significant in a number of respects: (i) the proposed spontaneous α-abstraction/elimination step is a fundamental process in organometallic chemistry but is still quite rare for the later transition elements; (ii) the migratory insertion of a methylidene[11] to a terminal phosphide moiety is a

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(11) Trapping of in situ generated iridium methylidene complexes has been reported in the following: Thorn, D. L. *Organometallics* **1985**, *4*, 192 and references therein.

new reaction; and (iii) the difference in the thermal and photochemical reaction pathways is both remarkable and curious and contrasts our previous report[4] on the formation of a stable methylidene under photochemical conditions only. Mechanistic studies[12] are in progress.

Acknowledgment. Financial support was provided by NSERC in the form of an operating grant to M.D.F. We also thank Johnson Matthey for the generous loan of $IrCl_3$.

Supplementary Material Available: NMR and analytical data for $Ir(\eta^2\text{-}CH_2PR_2)H[N(SiMe_2CH_2PPh_2)_2]$ (R = Ph, **2a**; R = Me, **2b**) (1 page). Ordering information is given on any current masthead page.

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(12) Preliminary kinetic investigations have established that both **1a** and **1b** rearrange via a first-order process; monitoring the disappearance of **1a**-d_3, $Ir(CD_3)PPh_2[N(SiMe_2CH_2PPh_2)_2]$, established that k_H/k_D is 1.42 (2). The thermolysis of the monodeuterated derivative $Ir(CDH_2)PPh_2[N(SiMe_2CH_2PPh_2)_2]$, **1a**-$d_1$, gives the corresponding hydride *fac*-$Ir(\eta^2\text{-}CHDPPh_2)H[N(SiMe_2CH_2PPh_2)_2]$ and the deuteride *fac*-$Ir(\eta^2\text{-}CH_2PPh_2)D[N(SiMe_2CH_2PPh_2)_2]$ in a ratio of 84 ± 2:16 ± 2, which corresponds to $k_H/k_D = 2.7$ (4) for the C–H cleavage step after correction for statistical effects and isotopic purity.

Stereomemory within a Formally Unsaturated Chiral Tungstenocene Methyl Complex

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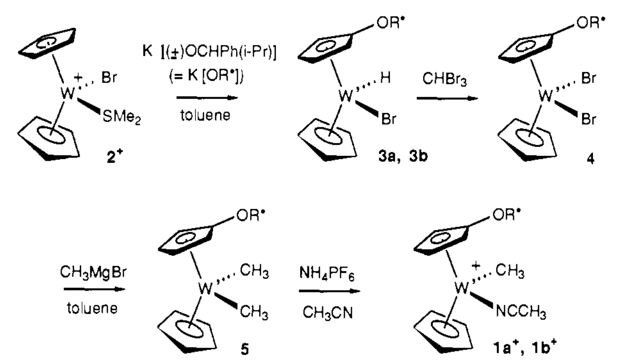
Chiral metal centers are important as stereochemical probes in mechanistic organometallic chemistry[3] and are of particular current interest because of the dramatic advances in chiral induction with organometallic reagents and catalysts.[4] When chiral centers are tetrahedrally coordinated they are usually stereochemically stable, and, when racemization occurs, it is dissociative and involves unsaturated intermediates.[3] Racemization does not, however, necessarily follow dissociation, and our understanding of chiral tetrahedral complexes would be advanced by elucidation of the factors controlling the stereochemistry of their unsaturated derivatives.[5] Alkyl complexes are particularly intriguing since they can achieve effective saturation via agostic interactions[6] or via α- or β-hydride elimination.[7] We recently developed a route to tungstenocene complexes with chiral metal centers,[8] and we now report how these may be used to determine the stereochemical stability of a formally unsaturated tungstenocene methyl complex.

Scheme I



The chiral tungstenocene methyl complex $[W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4OCHPh(i\text{-}Pr)\}(CH_3)(NCCH_3)]PF_6$ was prepared as an enantiomeric mixture of diastereomers (**1a**PF_6, **1b**PF_6)[9,10] from $[W(\eta\text{-}C_5H_5)_2(SMe_2)Br]PF_6$ (**2**PF_6) in four steps as shown in Scheme I. Crude $[W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4OCHPh(i\text{-}Pr)\}HBr]$ (**3a**, **3b**)[8,9] (prepared from 3.0 g, 5.0 mmol of **2**PF_6) was treated with bromoform (5 mL, 57 mmol) to precipitate analytically pure grey green crystals of $[W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4OCHPh(i\text{-}Pr)\}Br_2]$ (**4**,[11] 1.90 g, 3.05 mmol ≡ 61% from **2**PF_6) over 8 h. Methylation of **4** (0.225 g, 0.36 mmol) in toluene (45 mL) with 3.1 M MeMgBr in Et_2O (1.2 mL, 3.7 mmol) gave $[W(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4OCHPh(i\text{-}Pr)\}Me_2]$ (**5**) after 12 h. Pure **5**[12] (0.125 g, 0.25 mmol ≡ 71%) was isolated as orange needles by crystallization from pentane after ethanolysis. Protonolysis of **5** (0.085 g, 0.17 mmol) with NH_4PF_6 (0.080 g, 0.49 mmol) in CH_3CN (25 mL) for 5 h gave a 3:2 mixture (^1H NMR) of **1a**PF_6 and **1b**PF_6 (0.087 g, 0.13 mmol) in 77% yield after recrystallization (acetone/H_2O).

The less soluble diastereomer was separated from the mixture (1.5:1, 0.050 g, 0.075 mmol) by vigorously stirring (8 h) the oily orange brown solid in benzene (12 mL) to give a fine amber powder (>98% **1a**PF_6, 0.016 g, 0.024 mmol ≡ 53% of starting **1a**PF_6) under a red brown solution (0.72:1 **1a**$^+$ to **1b**$^+$).[13] Pure **1b**PF_6 could not be isolated by chromatography, fractional crystallization, or preferential extraction.

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(1) Harvard University.

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(7) See leading references in the following: McNally, J. P.; Cooper, N. J. *Organometallics* **1988**, *7*, 1704–1715.

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(9) In the case of complexes prepared as diastereomeric mixtures the "a" diastereomer is that with the downfield resonance for the C_5H_5 ligand in acetone-d_6. The absolute stereochemistries of the "a" and "b" diastereomers reported in this paper have not been determined and are not required for the present work.

(10) ^1H NMR $\{(CD_3)_2CO$, 500 MHz$\}$: **1a**PF_6 δ 7.3–7.5 (*c*, 5 H, C_6H_5), 5.32 (s, 5 H, C_5H_5), 5.29, 4.63, 4.51, 4.41 (m, 1 H each, C_5H_4), 4.92 (d, J = 5.9 Hz, 1 H, OCH), 2.68 (s, 3 H, $NCCH_3$), 2.25 (octet, J = 6.3 Hz, 1 H, $CH(CH_3)_2$), 1.00 (d, J = 6.9 Hz, 3 H, $CHCH_3$), 0.83 (d, J = 6.8 Hz, 3 H, $CHCH'_3$), 0.23 (s, satellites $J_{W\text{-}H}$ = 5.5 Hz, 3 H, W–CH_3); **1b**PF_6 δ 7.3–7.5 (c, 5 H, C_6H_5), 5.29 (s, 5 H, C_5H_5), 5.02 (d, J = 6.0 Hz, 1 H, OCH), 4.95, 4.87, 4.79, 4.61 (m, 1 H each, C_5H_4), 2.62 (s, 3 H, $NCCH_3$), 2.25 (m, 1 H, $CH(CH_3)_2$), 1.02 (d, J = 6.9 Hz, 3 H, $CHCH_3$), 0.80 (d, J = 7.0 Hz, 3 H, $CHCH'_3$), 0.19 (s, satellites $J_{W\text{-}H}$ = 5.5 Hz, 3 H, WCH_3). Anal. Calcd for $C_{23}H_{28}ONWPF_6$: C, 41.65; H, 4.26; N, 2.11. Found (Multichem, Lowell MA): C, 41.68; H, 4.22; N, 2.00.

(11) ^1H NMR $\{(CD_3)_2SO$, 250 MHz$\}$ δ 7.2–7.5 (c, 5 H, C_6H_5), 5.51 (s, 5 H, C_5H_5), 5.32, 5.08, 4.80, 4.40 (m, 1 H each, C_5H_4), 4.92 (d, J = 6.0 Hz, 1 H, OCH), 2.22 (m, 1 H, $CHCH_3$), 0.85 (d, J = 7.2 Hz, 3 H, $CHCH_3$), 0.72 (d, J = 7.2 Hz, 3 H, $CHCH'_3$); mass spectrum, parent ion: WBr_2 isotope envelope at m/e = 624 ($^{187}W^{81}Br_2$). Anal. Calcd for $C_{20}H_{22}OBr_2W$: C, 38.61; H, 3.57. Found (Multichem, Lowell MA): C, 38.56; H, 3.62.

(12) ^1H NMR $\{(CD_3)_2CO$, 250 MHz$\}$ δ 7.25–7.45 (c, 5 H, C_6H_5), 4.65 (d, J = 6.8 Hz, 1 H, OCH), 4.44 (s, 5 H, C_5H_5), 4.17, 3.87, 3.73, 3.64 (m, 1 H each, C_5H_4), 2.11 (octet, J = 7.0 Hz, 1 H, $CH(CH_3)_2$), 0.95 (d, J = 7.2 Hz, 3 H, $CHCH_3$), 0.79 (d, J = 7.2 Hz, 3 H, $CHCH'_3$), –0.15 (s, satellites $J_{W\text{-}H}$ = 6.0 Hz, 3 H, W-CH_3), –0.16 (s, satellites $J_{W\text{-}H}$ = 6.0 Hz, 3 H, W-CH'_3); $^{13}C\{^1H\}$ NMR $\{(CD_3)_2CO$, 75.5 MHz, DEFT sequence$\}$ δ 128.98, 128.53, 128.30 C_6H_5, non-ipso carbons), 87.83 (OCH), 87.02 (C_5H_5), 83.35 (C_5H_4, substituted carbon), 76.77, 71.30, 70.88, 69.36 (C_5H_4, nonsubstituted carbons), 35.49 ($CHCH_3$), 19.32 ($CHCH_3$), 18.48 ($CHC'H_3$), –17.20 (W–CH_3 satellites $J_{W\text{-}C}$ = 68 Hz), –19.14 (W–$C'H_3$ satellites $J_{W\text{-}C}$ = 74 Hz), mass spectrum, parent ion: W isotope envelope at m/e = 492 (^{184}W). Anal. Calcd for $C_{22}H_{28}OW$: C, 53.67; H, 5.74. Found (Multichem, Lowell MA): C, 53.42; H, 5.82.

(13) Further crops of **1a** could be obtained from the benzene extract by epimerization in CH_3CN at 60 °C for several hours followed by a further benzene extraction.

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