the absorption at 2010 cm^{-1} (characteristic of $Ir(CO)_3(PPh_3)_2{}^+BPh_4{}^-$ in solution) was strong, providing further confirmation of the identity of the intermediate. Conductance data on the reaction mixture from carbonylation of *trans*-$PhOIr(CO)(PPh_3)_2$ also indicate the formation of ionic species.[27]

The formation of the formates from alkoxides at the iridium upon carbonylation is best described as a displacement followed by nucleophilic attack on the cationic carbonyl complex.[28]

$$\textit{trans}\text{-}MeOIr(CO)(PPh_3)_2 + CO \rightarrow [Ir(CO)_2(PPh_3)_2OMe] \xrightarrow{CO} [Ir(CO)_3(PPh_3)_2]^+OMe^- \rightarrow MeOC(O)Ir(CO)_2(PPh_3)_2$$

The nucleophilic attack on a cationic carbonyl has ample literature precedence.[24,29] This mechanism is in contrast to either a MeO$^-$ migration (within the coordination sphere of the iridium) or a CO insertion but is consistent with the observation of $Ir(CO)_3(PPh_3)_2{}^+$ as an intermediate in the carbonylation. The step that leads to the conversion of the alkoxy into a carboalkoxy is the well-documented nucleophilic attack on the carbon of the coordinated carbon monoxide and has been previously demonstrated for MeO$^-$ attack on $Ir(CO)_3(PPh_3)_2{}^+$.[24] It is surprising that the alkoxide could be so readily displaced and that the reaction can proceed cleanly in high yield.

The methoxy complex had previously been reported to be unstable,[30] but in the absence of H_2O it is a quite stable complex. The preparation of the alkoxyiridium complexes require dried solvents and reagents. In the presence of H_2O the hydroxy complex is readily formed.

$$\textit{trans}\text{-}MeOIr(CO)(PPh_3)_2 + H_2O \rightarrow \textit{trans}\text{-}HOIr(CO)(PPh_3)_2 + CH_3OH$$

The hydroxy complex is a light yellow powder with ν(CO) at 1925 cm^{-1} and ν(OH) at 3600 cm^{-1} in KBr. Use of D_2O leads to trans-$DOIr(CO)(PPh_3)_2$ with a ν(OD) of 2658 cm^{-1}. The hydroxy complex does not react with CO under conditions similar to the methoxy analogue, indicating a stronger iridium–oxygen bond for the hydroxy complex.

The displacement, nucleophilic attack mechanism for the carbonylation of *trans*-$ROIr(CO)(PPh_3)_2$ suggests a careful reexamination of carbonylation of metal–oxygen bonds may be necessary. It also offers a new possibility for reaction of alkenes or alkynes with metal–oxygen bonds.

Acknowledgment. We thank Johnson Matthey, Inc., for a generous loan of $IrCl_3 \cdot xH_2O$, the donors of the Petroleum Research Fund, administered by the American Chemical Society for partial support of this research, the Alfred P. Sloan Foundation for a fellowship to J.D.A., and the Graduate School, SUNY at Buffalo, for a fellowship to W.M.R.

Registry No. $[Ir(CO)_3(PPh_3)_2]^+OPh^-$, 94070-37-8; $[Ir(CO)_3(PPh_3)_2]^+OPr^-$, 94070-36-7; $[Ir(CO)_3(PPh_3)_2]^+OMe^-$, 94070-35-6; $[Ir(CO)_3(PPh_3)_2]^+ClO_4{}^-$, 15738-08-6; $[Ir(CO)_3(PPh_3)_2]^+BPh^{4-}$, 59809-88-0; *trans*-$MeOIr(CO)(PPh_3)_2$, 94070-38-9; *trans-n*-$PrOIr(CO)(PPh_3)_2$, 94070-39-0; *trans*-$PhOIr(CO)(PPh_3)_2$, 94070-40-3; $MeOC(O)Ir(CO)_2(PPh_3)_2$, 15522-78-8; $PrOC(O)Ir(CO)_2(PPh_3)_2$, 63397-73-9; $PhOC(O)Ir(CO)_2(PPh_3)_2$, 94070-41-4; *trans*-$HOIr(CO)(PPh_3)_2$, 32356-70-0; *trans*-$DOIr(CO)(PPh_3)_2$, 94070-42-5; *trans*-$ClIr(CO)(PPh_3)_2$, 59246-46-7.

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(27) Conductance data were obtained in THF from a platinum black dipping electrode with a Sybron/Barnstead conductivity bridge (Model PM-70 CB) on 5 × 10^{-3} M solutions at 25 °C.

sol	$\overline{L}$, Ω^{-1} cm^{-1}
THF	$<8.86 \times 10^{-8}$ [a]
THF, CO	$<8.86 \times 10^{-8}$ [a]
$PhOIr(CO)(PPh_3)_2$	$<8.86 \times 10^{-8}$ [a]
$PhOIr(CO)(PPh_3)_2$, CO	1.95×10^{-6}
$Ir(CO)_3(PPh_3)_2BPh_4$	9.46×10^{-5}

[a] Below the limits of detection for instrument.

(28) With the current data we cannot rule out two competing mechanisms, only state that some portion proceeds through the cation.

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(30) Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1370.

η^2-Acyl Complexes of Group 4 Metals and of Actinides[†]

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Summary: The electronic and geometrical structure and reactivity of η^2-acyl complexes of group 4 transition metals and of actinides is the subject of this paper. We find and rationalize the preference for the O-inside η^2-acyl conformer of Ti and Zr bis(cyclopentadienyls) and approximately equal energy O-outside and O-inside conformers for the related U and Th complexes. We also find an unexpected η^1 minimum in the O-outside surfaces. This η^1-acyl can serve as an intermediate in the interconversion of the two η^2 isomers.

The carbonylation chemistry of bis(cyclopentadienyl) dialkyls or diaryls, haloalkyls, and related derivatives of group 4 d metals[1] and of actinides[2,3] shows many interesting facets. The isolable CO insertion products all

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[†] Dedicated to Prof. Günther Wilke on his 60th birthday.

(1) (a) $Cp_2Ti(COCH_3)Cl$ was formed by the reaction between $Cp_2Ti(CO)_2$ and CH_3COCl, Fachinetti, G; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946–1950. (b) Fachinetti, G.; Floriani, C.; Stöckli-Evans, H. *Ibid.* **1977**, 2297–2302. (c) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103–109 and references therein. (d) Wolczanski, P. T.; Bercaw, J. E. *Ibid.* **1980**, *13*, 121–127 and references therein. (e) Jeffery, J.; Lappert, M. F.; Luong-Thi, M. T.; Webb, M. *J. Chem. Soc., Dalton Trans.* **1981**, 1593–1605. (f) Baldwin, J. C.; Keder, N. L.; Strouse, C. E.; Kaska, W. C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1289–1297. (g) Klei, E.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *222*, 79–88. (h) Calderazzo, F. *Angew. Chem.* **1977**, *89*, 305–317; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299–311.

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(3) (a) For a CO insertion into the U═C double bond in $Cp_3UCHP(CH_3)(C_6H_5)_2$, see: Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1982**, *1*, 869–871. (b) Remarkably facile CO insertion into M–C and M–N bonds has also been found for Cp_3ThR, Cp_3UR, and Cp_3UNR_2: Sonnenberger, D. C.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 3484–3491. Paolucci, G.; Rossetto, G.; Zanella, P.; Yünlü, K.; Fischer, R. D., submitted for publication. For isocyanide insertions into U–C bonds see: Dormond, A.; Elbouadili, A. A.; Moise, C. *J. Chem. Soc., Chem. Commun.* **1984**, 749–751. For isocyanide insertions into Zr–R bonds (R = H, CH_3) of $Cp_2{}^*ZrR_2$: Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450–6452.

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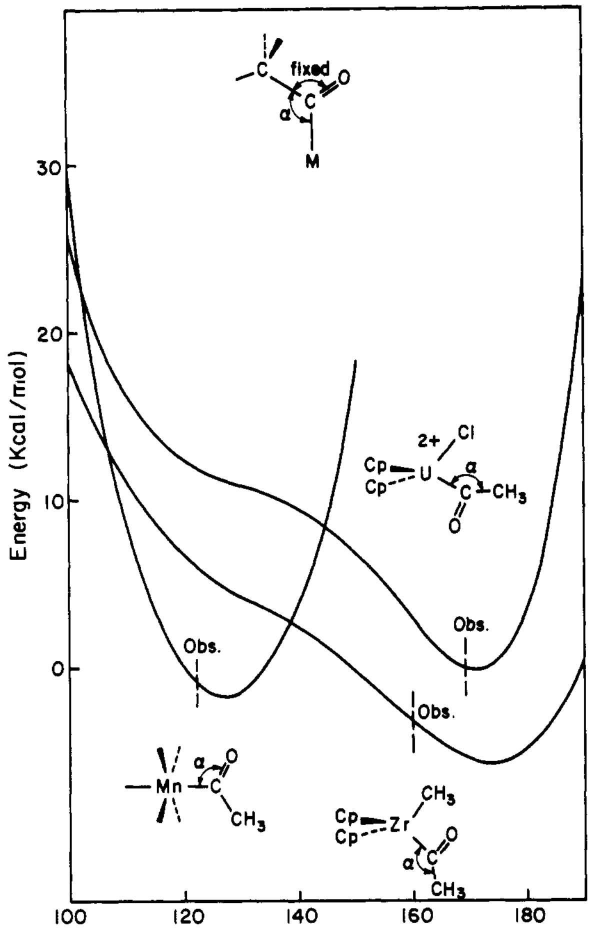
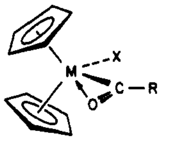


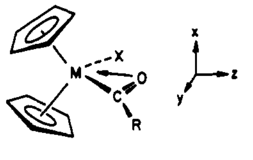
Figure 1. Potential energy curves for bending of an acyl ligand of $Cp_2Zr(COCH_3)(CH_3)$, $Cp_2U(COCH_3)Cl^{2+}$, and $Mn(CO)_5COCH_3$. Each curve is referred to an arbitrary zero of energy. Thus there is no interrelation in absolute energy between the curves.

contain η^2-acyl groups RCO, where both carbon and oxygen atoms are bound to a metal center. The unique reactivity of the coordinated acyls has been attributed to this η^2-bonding mode. Yet there are two possible isomeric structures in the η^2-acyl complexes: O-outside **1** and O-inside **2**. The acyl complexes of group 4 d metals $Cp_2Ti(COCH_3)Cl$[1a] and $Cp_2Zr(COCH_3)(CH_3)$[1b] show structures of type **2**, while the acyl ligand in the thorium



η^2-acyl O-outside

1



η^2-acyl O-inside

2

analogue $Cp^*_2Th(COCH_2$-t-$Bu)Cl$ [$Cp^* = C_5Me_5$] tends to orient as in **1**.[2c] For the related molecules $Cp^*_2M(CONR_2)Cl$ [M =Th, U] both conformers are in equilibrium,[2d] and $Cp_2{}^*Th(COPh)Cl$ has structure **2**.[2e] We focus our discussion here on the CO insertion process of Cp_2MRX and the novel structure of the η^2-acyl products.

Extended Hückel[4] energy curves for acyl pivoting of $Cp_2Zr(COCH_3)(CH_3)$ and $Cp_2U(COCH_3)Cl^{2+}$ are shown in Figure 1, which for comparison provides the energy of an acyl ligand in $Mn(CO)_5(COCH_3)$ so rotated.[5] The variable is the $M-C-CH_3$ angle α, while the other geometrical parameters of each complex are fixed. With a 2+ charge, the uranium complex assumes the $5f^06d^0$ configuration and can be regarded as a model of $Cp^*_2Th(COCH_2$-t-$Bu)Cl$, although the $5f^26d^0$ configuration also gives a potential curve very similar to that of the 2+ model.

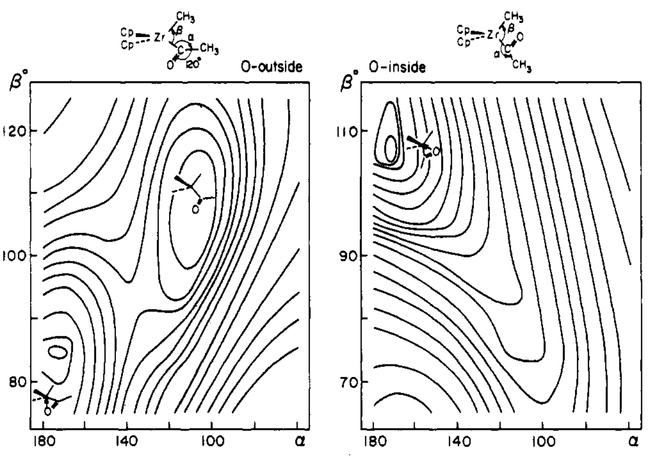
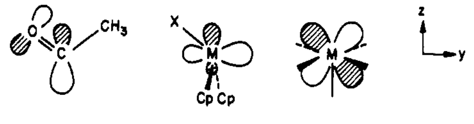


Figure 2. Potential energy surfaces for variation of the two angles, α(Zr-C-CH_3) and β(C-Zr-C), in O-inside (right) and O-outside (left) geometries of $Cp_2Zr(COCH_3)(CH_3)$.

For $Mn(CO)_5(COCH_3)$, the optimum mode of the acyl coordination is the η^1-type (α = 128°). On the other hand, the acyls of the Zr and U complex clearly distort toward η^2 geometries. These observations accord well with the X-ray structures.

The diversity of the bonding angle α is traced to interactions between the acyl(1−) lone-pair combination n_- (**3**) and the metal "d_π" orbitals (**4** and **5**). For $Cp_2Zr(CH_3)^+$



occ. unocc. occ.

3 **4** **5**

and Cp_2UCl^{3+}, the attractive interaction between the occupied n_- and vacant "d_π" orbitals is optimum in η^2 structures. In the latter case, an additional attractive interaction between n_- and vacant U f orbitals exists. In contrast, "d_π" of $Mn(CO)_5{}^+$, **5**, is occupied, and its interaction with the occupied n_- turns out to be repulsive, thus preventing the acyl groups from pivoting toward an η^2-form.

To compare stabilities between the O-outside **1** and O-inside **2** geometries of $Cp_2Zr(COCH_3)(CH_3)$, we show in Figure 2 two potential energy surfaces as a function of the angular parameters α(Zr−C−CH_3) and β(C−Zr−C). The potential minimum for **2** comes at α = 170° and β = 106°, which is approximately 5 kcal/mol more stable than the O-outside η^2 geometry **1** of α = 170° and β = 85°. Please recall that the X-ray structures of $Cp_2Zr(COCH_3)CH_3$ and

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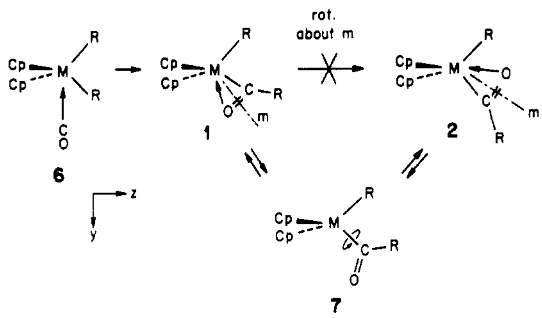
[4] Atomic parameters are as follows. H_{ii}: Zr 5s, −9.87 eV; Zr 5p, −6.76 eV; Zr 4d, −11.18 eV; Mn 4s, −8.63 eV; Mn 4p, −5.06 eV; Mn 3d, −11.59 eV. Orbital exponents: Zr 5s, 1.817; Zr 5p, 1.776; Zr 4d, 3.835 (0.62105) + 1.505 (0.57963); Mn 4s, 1.80; Mn 4p, 1.80; Mn 3d, 5.15 (0.5311) + 1.90 (0.6479). The *U* parameters are taken from: Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1980**, *19*, 2656–2658.

[5] There are many studies on the carbonylation of $RMn(CO)_5$ to give $RCOMn(CO)_5$. For example: Closson, R. D.; Kozikowski, J.; Coffield, T. H. *J. Org. Chem.* **1957**, *22*, 598. Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101–104. The η^1-acyl structure was observed by X-ray analysis for the related molecules: *cis*-$(CO)_4Mn(COCH_3)(COC_6H_5)$, Casey, C. P.; Bunnell, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 436–441; $(CO)_5MnCOCOCH_3$; Casey, C. P.; Bunnel, C. A.; Calabrese, J. C. *Ibid.* **1976**, *98*, 1166–1171.

Scheme I



$Cp_2Ti(COCH_3)Cl$ are indeed of type **2**. The orientational preference is again a consequence of a better 3–4 overlap in **2**. Calculations for the two acyl orientations of $Cp_2U(COCH_3)Cl^{2+}$ produced potential surfaces similar to those in Figure 2. In the U case, **1** was found to be more stable than **2**, but only slightly. The energy difference amounts to merely 0.7 kcal/mol. Not surprisingly, the two isomers of $Cp^*{}_2M(CONR_2)Cl$ (M = Th, U) coexist either in solution or in the crystal.

The most striking feature of the potential energy surfaces in Figure 2 is the presence of *two* minima for the O-outside structure.[6] One is for the aforementioned η^2 type, and the other corresponds to an η^1 coordination appearing at $\alpha = 110°$ and $\beta = 105°$. This observation is important in considering a pathway for CO insertion into M–R bonds.

It has been predicted that the initial attack of CO on Cp_2MR_2 (M = Ti, Zr) occurs from the y direction as indicated in **6** in Scheme I.[7] Our detailed calculations on $Cp_2M(CH_3)_2$ + CO (M = Zr, U) have reached the same conclusion. The puzzling question then arose as to why only product **2** had been isolated for the Zr system, instead of the immediate product **1**. Subsequently a fleeting intermediate, very possibly **1**, has been noted in the reaction of $Cp_2Zr(p\text{-}CH_3C_6H_4)_2$ with CO, which then isomerizes irreversibly to the thermodynamically more stable structure **2**.[8] However, direct rotation of an η^2-acyl about the axis m, as shown in Scheme I, is not likely because strong bonds between ligands and a bent Cp_2M fragment are formed only when the coordination occurs in the yz plane.[7] In fact the calculated barrier to the rotation from **1** to **2** was as high as ~50 kcal/mol for the Zr complex. How then does the isomerization take place? We propose an alternative route via the η^1 O-outside intermediate **7**, which was found in our potential surface. The transformation of **1** to **7** is an easier process, requiring an activation energy of only 7.5 kcal/mol for $Cp_2Zr(COCH_3)(CH_3)$. The following step from **7** to **2** involves a rotation of η^1-acyl about the M–C single bond, which could be a free rotation if steric problems did not hamper it. The calculated rotational barrier from **7** amounts to 8.5 kcal/mol which, together with the calculated energy difference of 5 kcal between η^1 and η^2 O-outside minima, results in a computed barrier of 13.5 kcal for O-outside to O-inside rearrangement. The experimentally observed $\Delta G^‡$ for the isomerization of $Cp_2Zr(COR)(R)$ ranges from 11.3 kcal/mol (R = CH_3) to 15.7 kcal/mol (R = p-tolyl, p-anisyl).[8]

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie (P.H. and P.S.) and to the National Science Foundation (R.H. and K.T.) for financial support. We also thank Dr. G. Erker for informative discussions.

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[6] A similar double minimum was calculated for $Cp_2Zr(CH_2PH_2)Cl$ or $Cp_2Zr(S_2CH)Cl$. (a) Hofmann, P.; Stauffert, P.; Schore, N. E. *Chem. Ber.* **1982**, *115*, 2153–2174. (b) Silver, M. E.; Eisenstein, O.; Fay, R. C. *Inorg. Chem.* **1983**, *22*, 759–770.

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Mechanism of Olefin Insertion into Metal-Oxygen Bonds. Reaction of $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Pt(CH_3)(OCH_3)$ with Tetrafluoroethylene[†]

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Summary: The reaction of (DPPE)Pt(CH_3)(OCH_3) [DPPE = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; bis(1,2-diphenylphosphino)ethane] (**1**) with tetrafluoroethylene (TFE) in THF-d_8 to form (DPPE)Pt(CH_3)($CF_2CF_2OCH_3$) (**2**) is first order in **1** and in TFE over a wide range of olefin concentrations ($\Delta H^‡$ = 12.5 kcal/mol and $\Delta S^‡$ = −32 eu). NMR measurements show no loss of ^{31}P or ^{195}Pt couplings to the methoxide protons in **1**, and **1** is insoluble in methanol. Thus methoxide does not dissociate from the starting material prior to forming **2**. Crossover experiments rule out a reaction mechanism involving charged intermediates arising from methoxide dissociation at any stage. At −80 °C the change in ^{19}F chemical shift of TFE was found to vary linearly with the quantity [**1**] [TFE], indicating that TFE and **1** interact, in preequilibrium fashion, to form a five-coordinate olefin complex as an intermediate in this reaction. Rate-limiting TFE insertion into the Pt–O bond of **1** follows at modest temperatures.

The sometimes severe conditions required for acid-catalyzed olefin hydration make a transition metal catalyzed route attractive. Of the steps necessary for catalytic olefin hydration,[1] only the coordination of an olefin to a hydroxo complex and the subsequent olefin insertion into its metal–oxygen bond are unknown.[2] The recently re-

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[†] Contribution No. 3550.

[1] A catalytic olefin hydration might involve (a) initial activation of an OH bond in water by a low-valent metal, (b) coordination of an olefin, followed by (c) olefin insertion into the M–O bond of the hydrido–hydroxo complex thus generated, and finally (d) the reductive elimination of product alcohol from a cis alkyl hydride to regenerate the low-valent metal catalyst. Step a is well precedented as is step d. (a) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027–38. (b) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941–3942. (c) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119–35. (d) Jones, R. F.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1981**, 58–9. (e) Halpern, J.; Abis, L.; Santi, R. *J. Organomet. Chem.* **1981**, *215*, 263–7. (f) Halpern, J.; Sen, A.; Abis, L. *J. Am. Chem. Soc.* **1978**, *100*, 2915–6. (g) Balazs, A. C.; Johnson, K. H.; Whitesides, G. M. Report TR-14; order #AD-A096 408; 1981. (h) Hill, R. H.; Puddephatt, R. J. *Inorg. Chim. Acta* **1981**, *54*, L277–L278. (i) Sostero, S.; Traverso, O.; Ros, R.; Michelin, R. A. *J. Organomet. Chem.* **1983**, *246*, 325–9.

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