the absorption at 2010 cm\(^{-1}\) (characteristic of Ir(CO)\(_3\) (PPh\(_3\))\(_2\)BPh\(_3\) \(_{-}\) 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.\(^{28}\) The displacement, nucleophilic attack mechanism for \(\text{MeO}^{-}\) migration (within the coordination sphere of the iridium) or a CO insertion but is consistent with the observation of \(\text{Ir(CO)}_3\) (PPh\(_3\))\(_2\) as an intermediate in the carbonylation. The step that leads to the conversion of the alkoxide into a carboalkoxy is the well-documented nucleophilic attack on the carbon of the coordinated carbon monoxide and has been previously demonstrated for \(\text{MeO}^{-}\) attack on \(\text{Ir(CO)}_3\) (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,\(^{20}\) but in the absence of \(\text{H}_2\text{O}\) it is a quite stable complex. The preparation of the alkoxyiridium complexes requires dioxanes and reagents. In the presence of \(\text{H}_2\text{O}\) the hydroxy complex is readily formed.

\[
\text{trans-MeOIr(CO)(PPh}_3\text{)}_2 + \text{CO} \rightarrow \nonumber \\
[\text{Ir(CO)}_3\text{(PPh}_3\text{)}_2\text{OMe}] \rightarrow \nonumber \\
\text{MeO(O)Ir(CO)}_3\text{(PPh}_3\text{)}_2
\]

The hydroxy complex is a light yellow powder with \(\nu(\text{CO})\) at 1925 cm\(^{-1}\) and \(\nu(\text{OH})\) at 3600 cm\(^{-1}\) in KBr. Use of \(\text{D}_2\text{O}\) leads to trans-DOIr(CO)(PPh\(_3\))\(_2\) with a \(\nu(\text{OD})\) 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 \(\text{trans-ROIr(CO)}(\text{PPh}_3\text{)}_2\) 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.

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Registry No. [Ir(CO)](PPh\(_3\))\(_2\)OPh, 94070-37-8; [Ir(CO)](PPh\(_3\))\(_2\)OPr, 94070-36-7; [Ir(CO)](PPh\(_3\))\(_2\)OMe, 94070-35-6; [Ir(CO)](PPh\(_3\))\(_2\)Cl, 15738-06-8; [Ir(CO)](PPh\(_3\))\(_2\)BPh\(_4\)\(_{-}\), 59809-88-0; trans-MeOIr(CO)(PPh\(_3\))\(_2\), 94070-38-9; trans-PrOIr(CO)(PPh\(_3\))\(_2\), 94070-39-0; trans-PhOIr(CO)(PPh\(_3\))\(_2\), 94070-40-3; MeO(O)Ir(CO)(PPh\(_3\))\(_2\), 15522-78-8; PrO(CO)(Ir(CO)(PPh\(_3\))\(_2\), 63397-73-9; PhO(CO)(Ir(CO)(PPh\(_3\))\(_2\), 94070-41-4; trans-HOIr(CO)(PPh\(_3\))\(_2\), 32556-70-0; trans-DIOIr(CO)(PPh\(_3\))\(_2\), 94070-42-5; trans-ClIr(CO)(PPh\(_3\))\(_2\), 89246-46-7.

\(\eta^2\)-Acyl Complexes of Group 4 Metals and of Actinides\(^{1}\)

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Summary: The electronic and geometrical structure and reactivity of \(\eta^2\)-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 \(\eta^2\)-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 \(\eta^2\) minimum in the O-outside surfaces. This \(\eta^2\)-acyl can serve as an intermediate in the interconversion of the two \(\eta^2\) isomers.

The carbonylation chemistry of bis(cyclopentadienyl) dialkyls or diaryls, haloalkyls, and related derivatives of \(\eta^2\)-transition metals’ and of actinides\(^{2-3}\) shows many interesting facets. The isolable CO insertion products all

\(^{1}\) Dedicated to Prof. Günther Wilke on his 80th birthday.

...(The rest of the text continues with the details of the research and findings, including references to specific compounds and reactions.)
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Figure 1. Potential energy curves for bending of an acyl ligand

Each curve is referred to an arbitrary zero of energy. Thus there

is no interrelation in absolute energy between the curves.

contain \( \eta^2 \)-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

\( \eta^2 \)-bonding mode. Yet there are two possible isomeric

structures in the \( \eta^2 \)-acyl complexes: 0-outside 1 and

0-inside 2. The acyl complexes of group 4 d metals

Cp\(_2\)Ti(COCH\(_3\))C\(_\text{l}\)\(_2\) and Cp\(_2\)Zr(COCH\(_3\))(CH\(_3\))\(_2\) show

structures of type 2, while the acyl ligand in the thorium

analogue Cp\(_*\)\(_2\)Th(COCH\(_3\)-t-Bu)C\(_\text{l}\)\(_2\) [Cp\(_*\) = C\(_5\)Me\(_5\)] tends to

orient as in 1.\(^2\) For the related molecules Cp\(_*\)\(_2\)M-

(CONR\(_2\))\(_2\)Cl [M = Th, U] both conformers are in equilib-

rium,\(^3\) and Cp\(_*\)\(_2\)Th(COPh)C\(_\text{l}\)\(_2\) has structure 2.\(^4\) We focus

our discussion here on the CO insertion process of

Cp\(_2\)MRX and the novel structure of the \( \eta^2 \)-acyl products.

Extended Hückel\(^4\) energy curves for acyl pivoting of

Figure 2. Potential energy surfaces for variation of the two angles,

\( \alpha(Zr-C-CH_3) \) and \( \beta(C-Zr-C) \), in O-inside (right) and O-outside (left) geometries of Cp\(_2\)Zr(COCH\(_3\))(CH\(_3\)).

Cp\(_2\)Zr(COCH\(_3\))(CH\(_3\)) and Cp\(_2\)U(COCH\(_3\))C\(_\text{l}\)\(_2\) 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 \( \alpha \), while the other geometrical pa-

rameters of each complex are fixed. With a 2+ charge, the

uranium complex assumes the 5f\(_0\)6d\(_0\) configuration and

can be regarded as a model of Cp\(_*\)Th(COCH\(_3\)-t-Bu)C\(_\text{l}\), al-

though the 5f\(_0\)6d\(_0\) configuration also gives a potential curve

very similar to that of the 2+ model.

For Mn(CO)\(_5\)(COCH\(_3\)), the optimum mode of the acyl

coordination is the \( \eta^1 \)-type (\( \alpha = 128^\circ \)). On the other hand,

the acyls of the Zr and U complex clearly distort toward

\( \eta^2 \) geometries. These observations accord well with the

X-ray structures.

The diversity of the bonding angle \( \alpha \) is traced to in-

teractions between the acyl(1-) lone-pair combination

\( n^- \) (3) and the metal \( \sigma^* \) orbitals (4 and 5). For Cp\(_2\)Zr(CH\(_3\))\(_2\)

and Cp\(_2\)UCl\(_2\), the attractive interaction between the oc-

cupied \( n^- \) and vacant \( \sigma^* \) orbitals is optimum in

\( \eta^2 \) structures. In the latter case, an additional attractive

interaction between \( n^- \) and vacant U f orbitals exists. In

contrast, \( \sigma^* \) of Mn(CO)\(_5\), 5, is occupied, and its inter-

action with the occupied \( n^- \) turns out to be repulsive, thus

preventing the acyl groups from pivoting toward an

\( \eta^2 \)-form.

To compare stabilities between the O-outside 1 and

O-inside 2 geometries of Cp\(_2\)Zr(COCH\(_3\))(CH\(_3\)), we show in

Figure 2 two potential energy surfaces as a function

of the angular parameters \( \alpha(Zr-C-CH_3) \) and \( \beta(C-Zr-C) \). The

potential minimum for 2 comes at \( \alpha = 170^\circ \) and \( \beta = 106^\circ \),

which is approximately 5 kcal/mol more stable than the

O-outside \( \eta^- \) geometry 1 of \( \alpha = 170^\circ \) and \( \beta = 85^\circ \). Please

recall that the X-ray structures of Cp\(_2\)Zr(COCH\(_3\))(CH\(_3\)) and

(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.


Chem. 1967, 10, 101–104. The \( \eta^- \) structure was observed by X-ray

analysis for the related molecules: cis(CO)\(_2\)Mn(COCH\(_3\))\(_2\)(COC\(_\text{H}_5\)), Ca-

sey, C. P.; Bunnell, C. A. J. Am. Chem. Soc. 1976, 98, 436-441; (CO)\(_5\)MnCO-

COCH\(_3\) Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. Ibid. 1976, 98, 1166-1171.
Cp₂Ti(COCH₃)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 Cp₂U(COCH₃)Cl² were performed 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 Cp₂M(CONR₂)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 π² type, and the other corresponds to an π¹ coordination appearing at α = 110° and β = 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 Cp₂MR₂ (M = Ti, Zr) occurs from the y direction as indicated in 6 in Scheme I.⁷ Our detailed calculations on Cp₂M(CH₃)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 Cp₂Zr(p-CH₃C₆H₄)₂ with CO, which then isomerizes irreversibly to the thermodynamically more stable structure 2.⁸ However, direct rotation of an π²-acyl about the axis m, as shown in Scheme I, is not likely because strong bonds between ligands and a bent Cp₂M 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 π¹ 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 Cp₂Zr(COCH₃)(CH₃). The following step from 7 to 2 involves a rotation of π¹-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 π² and π¹ O-outside minima, results in a computed barrier of 13.5 kcal for O-outside to O-inside rearrangement. The experimentally observed ΔG° for the isomerization of Cp₂Zr(COR)(R) ranges from 11.3 kcal/mol (R = CH₃) to 15.7 kcal/mol (R = p-tolyl, p-anisyl).⁸

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Mechanism of Olefin Insertion into Metal–Oxygen Bonds. Reaction of [(C₅H₅)₂PCH₂CH₂P(C₅H₅)₂]₂Pt(CH₃)(O₂CCH₂) with Tetrafluoroethylene

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Summary: The reaction of (DPPE)₂Pt(CH₃)(O₂CCH₂) with tetrafluoroethylene (TFE) in THF-d₅ to form (DPPE)₂Pt(CH₃)(CF₂CF₂OCH₂) (1) is first order in 1 and in TFE over a wide range of olefin concentrations (ΔH° = 12.5 kcal/mol and ΔS° = -32 eu). NMR measurements show no loss of ³¹P or ¹⁹F coupling 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 ¹⁹F chemical shift of TFE was found to vary linearly with the quantity [¹⁹F][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, only the coordination of an olefin to a hydroxo complex and the subsequent olefin insertion into its metal–oxygen bond are unknown. The recently re-

⁶A similar double minimum was calculated for Cp₂Zr(CH₃)₂Cl or Cp₂Zr(S₂CH)Cl. (a) Hofmann, P.; Stauffert, P.; Schore, N. E. Chem. Ber. 1982, 115, 2139-2174. (b) Silver, M. E.; Eisenstein, O.; Fay, R. C. Inorg. Chem. 1985, 24, 729-730.
