isostructural to C as well as η^3-1-azaallyl complexes[21] are well-documented.

To the best of our knowledge compounds 1 and 2 are the first examples of nickelacyclopentanes formed by coupling of two different olefines at the metal. There are only two other stable mixed metallacyclopentanes, namely, 4-(cyclopentadienyl)-4-(triphenylphosphane)-2,2-dimethyl-5-nitrilo-4-cobaltabicyclo[3.1.0]hexane[22] and a ferrabicylo[3.2.0]heptane derivative[23] known to date whose role as possible intermediates in catalytic processes has not been investigated. We have obtained evidence that the nickel complex 1 can be regarded as an intermediate in the above-mentioned cotrimerization reaction of dmcp and mac (eq 1); for a proposed mechanism of this reaction see ref 10. Like the "in situ" catalyst obtained by mixing $\mathrm{Ni(cod)_2}$ and tpp in the molar ratio of 1:1[10] compound 1 catalyzes the cotrimerization at ambient temperature. Both types of catalysts produce almost identical yields and compositions of compounds 3–5. But we have also found that 1 does not react at all with dmcp or mac alone. This indicates that a mixture of both olefins is necessary to achieve a catalytic cycle. Further experiments are necessary in order to understand these phenomena.

Acknowledgment. We are grateful to Dr. D. Henneberg and Dr. K. Seevogel for providing mass and IR spectra, respectively.

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Communications

Selectivity in C–O Bond Formation: Reaction of Acid Chlorides and Methyl Iodide with *trans*-$\mathrm{MeOIr(CO)(PPh_3)_2}$

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Summary: Reactions of RX (RX = MeI, $\mathrm{CH_3C(O)Cl}$, $\mathrm{C_6H_5C(O)Cl}$, and $\mathrm{C_6H_5CH_2C(O)Cl}$) with *trans*-$\mathrm{MeOIr(CO)(PPh_3)_2}$ have been examined. In each case, an adduct is formed, $\mathrm{RIr(OMe)(CO)(PPh_3)_2X}$, which is stable for R = Me. For the acid chlorides, this adduct eliminates ester, forming $\mathrm{Ir(CO)(PPh_3)_2Cl}$. Thus the carbon–oxygen bond leading to ester products is formed more readily than the carbon–oxygen bond leading to dimethyl ether.

Transition-metal acyl complexes are key to two of the most important applications of homogeneous catalysts, hydroformylation and methanol carbonylation.[1-5] Acyl complexes may be formed by carbonylation of alkyl complexes (alkyl migration processes) or by addition of acid chlorides or aldehydes to 16-electron complexes.[1-3] The reactions thus far reported for acyl complexes appear to be limited to decarbonylation,[6] reductive-elimination reactions (C–H, C–C, and C–I bond formation)[5,7-10] and the recent report of β-elimination.[11] In order to expand the known reactions of acyl groups, we have begun to examine possible carbon–oxygen bond formation through oxidative addition of acid chlorides to the alkoxide complex, *trans*-$\mathrm{MeOIr(CO)(PPh_3)_2}$.[12,13] These reactions lead to C–O bond formation with production of esters. Carbon–oxygen bond formation has been previously reported on Ni(II) and Pd(II).[14] Reaction with methyl iodide has also been examined as a comparison to the acid chlorides.

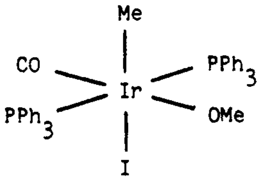

Figure 1. Suggested geometry for the MeI adduct with *trans*-$\mathrm{MeOIr(CO)(PPh_3)_2}$. This geometry is consistent with the spectroscopic parameters.

The reaction of acetyl chloride with *trans*-$\mathrm{MeOIr(CO)(PPh_3)_2}$ leads to $\mathrm{CH_3C(O)Ir(CO)(PPh_3)_2Cl_2}$ and $\mathrm{CH_3C(O)OMe}$ in high yield.[15]

$$trans\text{-}\mathrm{MeOIr(CO)(PPh_3)_2 + 2CH_3C(O)Cl \rightarrow CH_3C(O)Ir(CO)(PPh_3)_2Cl_2 + CH_3C(O)OMe}$$

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[15] A solution of 0.05 g of *trans*-$\mathrm{MeOIr(CO)(PPh_3)_2}$[13] in 5 mL of benzene was placed in a pressure tube fitted with a Teflon stopcock and brought out of the drybox. The tube was placed on a vacuum line and degassed, and 0.10 mL of purified acetyl chloride[16] was distilled onto the solution. The solution was stirred for 1 h, after which the solvent was removed by vacuum distillation and saved for further analysis. The white solid $\mathrm{CH_3C(O)Ir(Cl)_2(CO)(PPh_3)_2}$ (IR in KBr: 2060 (vs) and 1620 $\mathrm{cm^{-1}}$ (s)[17]) and, depending upon the purity of the acetyl chloride used and the care of the workup, $\mathrm{HIr(Cl)_2(CO)(PPh_3)_2}$ (IR in KBr: $\nu_{\mathrm{C{\equiv}O}}$ 2020 (vs) and $\nu_{\mathrm{Ir-H}}$ 2238 (s) $\mathrm{cm^{-1}}$) were formed. The distillate was analyzed for methyl acetate which was identified by IR and NMR (91% yield based on the Ir complex). Reactions of *trans*-$\mathrm{MeOIr(CO)(PPh_3)_2}$ with phenylacetyl chloride and benzoyl chloride were done by Schlenk techniques and analyzed similarly.

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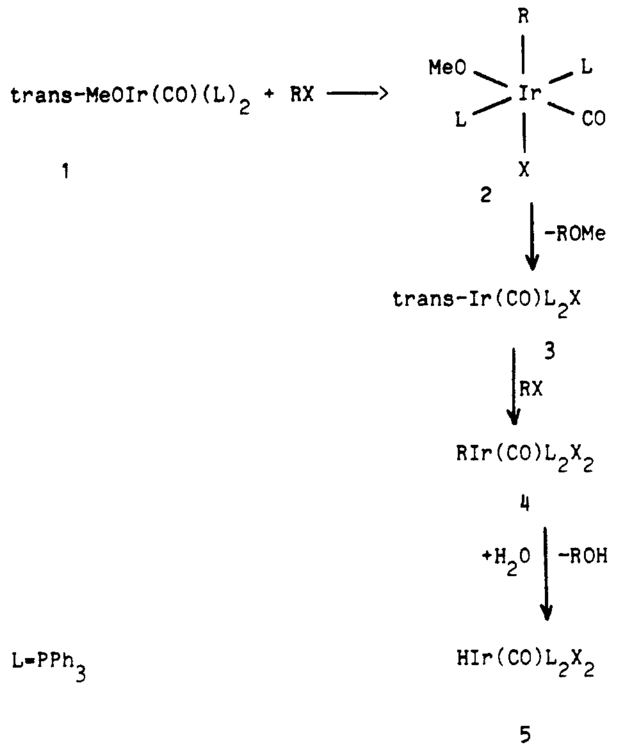

Figure 2. Scheme which summarizes the observed chemistry between RX and *trans*-MeOIr(CO)$(PPh_3)_2$. **2** has been isolated for MeI; ROMe is observed for R = $CH_3C(O)$, $C_6H_5C(O)$, and $C_6H_5CH_2C(O)$; **3** is the final product for $C_6H_5C(O)Cl$; **4** is the product for $CH_3C(O)Cl$ and $C_6H_5CH_2C(O)Cl$ under anhydrous conditions; **5** is observed to form from **4** with traces of water.

Analogous products were obtained from addition of phenylacetyl chloride. In both of these cases (but especially for $CH_3C(O)Cl$) care must be taken to avoid hydrolysis of the acetyl product to the hydride HIr(CO)$(PPh_3)_2Cl_2$. The reaction of benzoyl chloride with *trans*-MeOIr(CO)$(PPh_3)_2$ also leads to the ester $C_6H_5C(O)OMe$, but a second $C_6H_5C(O)Cl$ does not add to *trans*-Ir(CO)$(PPh_3)_2$Cl, as previously reported.[17]

In contrast to the acid chlorides, methyl iodide adds to *trans*-MeOIr(CO)$(PPh_3)_2$ to form a stable adduct.[18] The infrared and NMR data are consistent with the geometry shown in Figure 1. Preliminary results of an X-ray structure determination support this geometry.[19] To encourage elimination of dimethyl ether, we warmed (45 °C) a solution of MeIr(OMe)(CO)$(PPh_3)_2$I and opened a decomposition pathway that produces CH_4, CH_3OH, and *trans*-Ir(CO)$(PPh_3)_2$I in variable yields depending on the solvent, but in no case was dimethyl ether observed.

The chemistry which we have observed is summarized in Figure 2. **2** has been isolated for R = Me and X = I; **3** has been isolated for R = $C_6H_5C(O)$ and X = Cl; **4** has been isolated for R = $CH_3C(O)$ and $C_6H_5CH_2C(O)$ and X = Cl; and **5** has been isolated for R = $CH_3C(O)$ and $C_6H_5CH_2C(O)$ and X = Cl. The reactions of MeI and the acid chlorides with *trans*-MeOIr(CO)$(PPh_3)_2$ occur rapidly. Previous study has shown that oxidative addition of alkyl and acid halides to square-planar Ir(I) complexes occurs with a trans geometry as shown for **2**.[2,17]

Oxidative addition of acid chlorides and methyl iodide to *trans*-MeOIr(CO)$(PPh_3)_2$ leads to the formation of carbon–oxygen bonds giving esters but not ethers.[20] Details of these reactions, including variation of the alkoxy (R) groups, will be reported in the full paper.

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(16) Purification of acid chlorides: all acid chlorides used were purchased from Aldrich. Phenylacetyl chloride and benzoyl chloride were passed down a basic alumina column and used under a nitrogen atmosphere. Acetyl chloride was predried by stirring over basic alumina (14 h), then vacuum distilled onto *N*,*N*-dimethylaniline, and stirred 5 min. The first one-third portion of the acid chloride was distilled and discarded, and ~90% of the remaining portion was distilled into a pressure tube fitted with a Teflon stopcock and stored until needed. Glassware was oven-dried, and the vacuum apparatus was heated prior to use.

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(18) Ir(OMe)(Me)(CO)$(PPh_3)_2$I was prepared by addition of 0.20 mL of MeI to 0.25 g of *trans*-MeOIr(CO)$(PPh_3)_2$ in 40 mL of C_6H_6 under inert atmosphere. Stirring for 5 min and solvent removal led to a solid that was washed (2 × 10 mL of toluene, 2 × 20 mL of hexanes). The yield was 0.15 g (51%) of a white product with IR (1985 cm^{-1}) in KBr and ^{1}H NMR in benzene-d_6 (1.13 (t, J_{P-H} = 4.8 Hz), 3.37 (s), 7.0 (m) ppm) indicating correct formulation of the product. Microanal. Calcd: C, 51.03; H, 3.93. Found: C, 49.51; H, 3.50.

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(20) As suggested by a reviewer we cannot be certain at this point that a direct interaction of the acid chlorides with the methoxy group does not occur. In the absence of evidence that a direct reaction is occurring, we prefer to consider the known oxidative addition to a square-planar Ir(I) complex.[17]

1,8-Naphthalenediylbis(dichloroborane) Chloride: The First Bis Boron Chloride Chelate

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Summary: The synthesis and chloride complexing properties of 1,8-naphthalenediylbis(dichloroborane) are reported. This compound, prepared from 1,8-bis(chloromercurio)naphthalene and BCl_3, forms chelate complexes with inorganic and organic choride donors as determined by ^{11}B NMR. X-ray crystallography confirmed the presence of unprecedented B–Cl–B bridge bonds in the complexes.

We have already demonstrated[1] that 1,8-naphthalenediylbis(dimethylborane) (hydride sponge) forms stable, bridged complexes by abstracting H$^-$, F$^-$, and OH$^-$. On the other hand, it appeared from NMR data that the interaction of hydride sponge with Cl$^-$ is weak or nonexistent. Prompted by the recent interest in Cl$^-$ chelation by organotin[2] and organomercury[3] bidentate Lewis acids and the importance of chloride-abstracting Lewis

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