enough electron density in the axial positions to preclude coordination of axial ligands. Another point of contrast in the d^8d^7 structure versus d^7d^7 structures is the short RhRh distance. The RhRh bond (bond order $^1/_2$) in $[Rh(chp)(NBD)]_2^+$ (2.819 Å) is shorter than the RhRh (bond order 1) distance in $Rh_2(bridge)_4Cl_2^{2+}$ (2.837 Å) bridge = 1,3-diisocyanopropane). We attribute this apparent anomaly to a lenghthened Rh(II)–Rh(II) bond in the d^7d^7 bridge complex due to destabilization of the metal–metal bond via Rh–Cl axial bond formation.

Conclusions

The complex $[Rh(chp)(NBD)]_2$ has been prepared via a procedure previously found convenient for the preparation of $[Rh(hp)(COD)]_2$ and $[Ir(hp)(COD)]_2$. The neutral d^8–d^8 complex was isolated, characterized, and subjected to crystallographic analysis. $[Rh(chp)(NBD)]_2$ is composed of two intersecting square-planar Rh(I) centers bridged by the two hydroxypyridinate ligands. The molecule is structurally similar to the previously characterized $[M(mhp)(COD)]_2$ (M = Rh, Ir) complexes with nearly C_2 symmetry at the metals. The complex contains a relatively flexible eight-membered metallocycle ring and a shorter and stronger Rh–Rh interaction than the mhp complex. The smaller bite distance and steric requirements of NBD allow the Rh atoms to interact more strongly and allow the square planes to attain a dihedral angle of 49°.

The one-electron oxidation of $[Rh(chp)(NBD)]_2$ results in the formation of a stable radical complex, $[Rh(chp)(NBD)]_2^+$, that has been thoroughly characterized as a mixed-valence, paramagnetic complex. Crystallographic analysis indicates the removal of an electron from the metal–metal σ^* antibonding molecular orbital decreases the metal–metal distance to 2.819 Å, consistent with a bond order of one-half. The EPR spectrum of frozen CH_2Cl_2/TBAP solutions of $[Rh(chp)(NBD)]_2(PF_6)$ displays three signals at $g = 2.08$, 2.21, and 2.25 which correspond to random alignment of each molecular axis with the applied magnetic field.

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Registry No. $[Rh(chp)(NBD)]_2$, 118317-86-5; $[Rh(chp)(NBD)]_2(PF_6)$, 118299-44-8; $[Rh(NBD)Cl]_2$, 12257-42-0; Na(chp), 59432-71-2.

Supplementary Material Available: Tables of thermal parameters, hydrogen positions, bond lengths, bond angles, and least-squares planes (14 pages); listings of structure factors for $[Rh(chp)(NBD)]_2$ and $[Rh(chp)(NBD)](PF_6)\cdot CH_2Cl_2$ (29 pages). Ordering information is given on any current masthead page.

Reactions of Iridium(I) Alkoxide Complexes with Acyl and Alkyl Sources: Carbon–Oxygen Bond-Forming Reactions

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The reactions of alkoxyiridium complexes *trans*-$ROIr(CO)(PPh_3)_2$ (R = Me, Ph, *t*-Bu, *i*-Pr) with organic substrates R′X (R′ = Me, $CH_3C(O)$, $C_6H_5C(O)$, $C_6H_5CH_2C(O)$, HC(O); X = Cl, I, H) lead to esters ROR′ but not to ethers. Reaction of acid chlorides leads to $R'Ir(CO)(PPh_3)_2Cl_2$ and the ester. Reaction of aldehydes gives $HIr(CO)_2(PPh_3)_2$ and the ester ROR′ in addition to Tischenko products $R'CH_2C(O)OR'$. Reaction of MeI gives the six-coordinate adduct $MeOIr(Me)(I)(CO)(PPh_3)_2$ that does not eliminate dimethyl ether. Carbonylation and decomposition of $MeOIr(Me)(I)(CO)(PPh_3)_2$ leading to $MeOC(O)Ir(Me)(I)(CO)(PPh_3)_2$ and *trans*-$Ir(CO)(PPh_3)_2I$, respectively, are also reported.

Bond formation through reductive elimination is an important reaction in organometallic chemistry and homogeneous catalysis. Carbon–hydrogen and, to a lesser extent, carbon-carbon bond formation have been examined.[1-11] Relatively few studies of oxygen–hydrogen and oxygen–carbon bond formation have appeared.[12-15] Oxidative additions to *trans*-$MeOIr(CO)(PPh_3)_2$ offer the potential to examine the systematics of carbon–oxygen and oxygen–hydrogen bond formation.

We have previously reported carbon–oxygen bond formation by addition of acid chlorides to *trans*-$ROIr(CO)(PPh_3)_2$

$$trans\text{-}ROIr(CO)(PPh_3)_2 + 2R'C(O)Cl \rightarrow R'C(O)Ir(CO)(PPh_3)_2Cl_2 + R'C(O)OR \quad (1)$$

$$R = Me, Ph;\ R' = Me, CH_2C_6H_5$$

which lead to ester formation.[14] Esters were also observed as products by addition of aldehydes to the iridium alkoxides[15]

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$$trans\text{-}ROIr(CO)(PPh_3)_2 + 2R'CHO \rightarrow R'C(O)OR + HIr(CO)_2(PPh_3)_2 + R'H + R'CH_2C(O)OR' \quad (2)$$

In this case, formation of esters by dimerization of aldehyde (Tischenko products) was seen in addition to the ester from combination of the alkoxide and the aldehyde.

Carbon–oxygen bond formation has also been observed in reductive elimination of aryl carbonylates from Ni(II) and Pd(II).[13] Reaction of Fe(II) alkoxide complexes with acid chlorides and alkyl halides similarly led to formation of esters and ethers, respectively.[13] In this paper we report the full experimental details of the C–O bond-forming reactions of the alkoxide complexes *trans*-ROIr(CO)-$(PPh_3)_2$ with acid chlorides and aldehydes. We also report the synthesis of $MeOIr(Me)(I)(CO)(PPh_3)_2$, the spectroscopic characterization of this complex, and its decomposition and carbonylation.

Experimental Section

Iridium trichloride, $IrCl_3 \cdot xH_2O$, was purchased or loaned from Johnson Matthey Inc. All acid chlorides were purchased from Aldrich. Methyl iodide was purchased from Malinckrodt. Acetaldehyde was purchased from Aldrich, and paraformaldehyde was purchased from Fisher Scientific Co. All solvents were dried and degassed prior to use. All syntheses were accomplished under a nitrogen, argon, or vacuum atmosphere. Infrared spectra were recorded on a Beckman 4240, and ^1H NMR and ^{31}P NMR spectra were recorded on a Varian EM 390 or on a JEOL FX90Q. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Inc., Woodside, NY. Gas chromatography was performed on a Varian 2440-FID gas chromatograph.

Reaction of Acetyl Chloride with *trans*-MeOIr(CO)-$(PPh_3)_2$. A solution of 0.05 g of *trans*-MeOIr(CO)$(PPh_3)_2$ 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 acetyl chloride 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 $CH_3C(O)IrCl_2(CO)(PPh_3)_2$ (IR spectrum in KBr 2060 (vs) and 1620 (s) cm^{-1})[16] and depending upon the purity of the acetyl chloride used and the care of the workup $HIrCl_2(CO)(PPh_3)_2$ (IR spectrum in KBr 2238 (s) and 2020 (vs) cm^{-1})[17] were formed. The distillate was analyzed for methyl acetate which was identified by IR and NMR spectroscopy (91% yield based on the Ir complex).

Reaction of Acetyl Chloride with *trans*-PhOIr(CO)-$(PPh_3)_2$. *trans*-PhOIr(CO)$(PPh_3)_2$ (0.025 g) in 10 mL of cyclohexane was placed in a pressure tube and brought out of the drybox. The tube was placed on a vacuum line and degassed, and then 0.05 mL of acetyl chloride was distilled onto the solution. After the solution was stirred for 1 h, the solvent was removed and examined. The products were $CH_3C(O)IrCl_2(CO)(PPh_3)_2$ and $HIrCl_2(CO)(PPh_3)_2$, as for the methoxy complex. An IR spectrum of the distillate showed formation of $PhOC(O)CH_3$ (1713 cm^{-1}).

Reaction of Benzoyl Chloride with *trans*-MeOIr(CO)-$(PPh_3)_2$. *trans*-MeOIr(CO)$(PPh_3)_2$ (0.05 g) in 10 mL of benzene was placed in a Schlenk flask and brought out of the glovebox. Benzoyl chloride (0.05 mL) (purified through a basic alumina column) was added to the solution under nitrogen. The reaction was allowed to stir for 5 min. An IR spectrum of the solution (yellow) showed a change in the CO stretching frequency from 1935 (s) to 1960 (br) cm^{-1} which was attributed to *trans*-ClIr-(CO)$(PPh_3)_2$ formation. An NMR spectrum of the solution was taken directly due to the high boiling point of the acid chloride. The ^1H NMR of the solution showed 7–8 (m) and 3.65 (s) ppm. The peak at 3.65 ppm was attributed to PhC(O)OMe as compared to an authentic sample prepared via reaction of PhC(O)Cl with NaOMe in benzene.

Reaction of Phenylacetyl Chloride with *trans*-MeOIr-(CO)$(PPh_3)_2$. *trans*-MeOIr(CO)$(PPh_3)_2$ (0.10 g) was dissolved in 10 mL of benzene and placed in a Schlenk flask and brought out of the drybox. Phenylacetyl chloride (0.50 mL) was added to the solution under nitrogen. (The acid chloride had been previously purified on a basic alumina column.) The solution was allowed to stir for 2 h. An IR spectrum of the solution showed 2068 (vs), 2050 (vs), 1960 (m, br), 1743 (s), and 1640 (m) cm^{-1}. The solvent was removed to yield an off-white solid that was identified as $PhCH_2C(O)IrCl_2(CO)(PPh_3)_2$ based on the IR spectrum of the solid in benzene (2068 (vs) and 1640 (m) cm^{-1}) and comparison to an authentic sample.[16] The reaction was repeated under identical conditions for *trans*-ClIr(CO)$(PPh_3)_2$ with identical IR absorptions after 2 h with the exception of the peak at 1743 cm^{-1}, which corresponds to $PhCH_2C(O)OMe$, formed in nearly quantitative yield. Complete exclusion of water is necessary to avoid formation of $HIrCl_2(CO)(PPh_3)_2$.

Reaction of *trans*-MeOIr(CO)$(PPh_3)_2$ with $H_2C(O)$. In a drybox 0.10 g (0.129 mmol) of *trans*-MeOIr(CO)$(PPh_3)_2$ and 0.02 g of paraformaldehyde were placed in 10 mL of THF and the mixture was stirred. The reaction was monitored by IR spectroscopy. The appearance of a peak at 1727 cm^{-1} (methyl formate) occurred within 30 min of the beginning of the reaction and continued to grow. The IR spectrum also began to show broadening in the CO region within 8 h. The reaction was allowed to continue until no further change was evident in the IR spectrum (1 week). Further confirmation of methyl formate as the byproduct of the reaction was accomplished by analysis of the reaction distillate through ^1H NMR spectroscopy and gas chromatography. The ^1H NMR spectrum in benzene showed the expected singlet at 3.2 ppm, as compared to an authentic sample of HCO_2Me. Gas chromatography of the liquid also confirmed HCO_2Me formation, which was performed on a Varian 2440 FID, Carbowax 20M column at 60 °C. The solvent from the reaction solution was then removed to yield a yellow solid, which was chromatographed on Florisil and eluted with 1:4 THF/cyclohexane. The resulting yellow solid was identified as $HIr(CO)_2$-$(PPh_3)_2$.[18] An IR spectrum of the solid in cyclohexane showed: 2085 (m, br), 1993 (s), 1983 (m), 1945 (vs), 1935 (s) cm^{-1}. The reactions with *trans*-*n*-PrOIr(CO)$(PPh_3)_2$, *i*-PrOIr(CO)$(PPh_3)_2$, and *t*-BuOIr(CO)$(PPh_3)_2$ were accomplished under similar conditions. Characteristic IR bands for the expected formate products were seen in each case. The reaction of *trans*-*n*-PrOIr(CO)$(PPh_3)_2$ with H_2CO was also examined by ^1H NMR spectroscopy. The organic products were found to be methyl formate [3.2 (s) ppm] as well as *n*-propyl formate [3.76 (t), 1.28 (q), and 1.08 (t) ppm] by comparison to authentic samples. Similarly, the reaction of *trans*-*t*-BuOIr(CO)$(PPh_3)_2$ with $H_2C(O)$ was also examined by NMR spectroscopy. The organic products were found to be *tert*-butyl formate [1.1 (s) ppm] as well as methyl formate [3.2 (s) ppm]. Reaction of formaldehyde with *trans*-ROIr(CO)$(PPh_3)_2$ produces $CH_3OC(O)H$ in two turnovers and ROC(O)H in 90% yield after 2 days at room temperature.

Attempted Reaction of *trans*-PhOIr(CO)$(PPh_3)_2$ with $H_2C(O)$. In a drybox 0.050 g of *trans*-PhOIr(CO)$(PPh_3)_2$ and 0.01 g of paraformaldehyde in 10 mL of THF were stirred and monitored by IR spectroscopy. No sign of reaction was evident after 3 days.

Reaction of *trans*-MeOIr(CO)$(PPh_3)_2$ with CH_3CHO. Monitored by IR. A pressure tube fitted with a Teflon stopcock containing 0.05 g (0.065 mmol) of *trans*-MeOIr(CO)$(PPh_3)_2$ in 20 mL of cyclohexane was brought out of the drybox. The tube was degassed on a vacuum line after which 0.10 mL of CH_3CHO was distilled onto the reaction solution. The reaction was monitored by IR spectroscopy. After 3 h the IR spectrum showed 2018 (s), 1958 (vs), and 1668 (m) cm^{-1} in addition to (CH_3CHO) 1730 (vs, br) cm^{-1}. As the reaction was allowed to continue for several days, broadening in the CO region occurred with development of new peaks. After 3 days, the IR spectrum showed the formation of $HIr(CO)_2(PPh_3)_2$ as well as the peak at 1958 cm^{-1}. The presumed oxidative addition product had disappeared for the most part. Reaction of acetaldehyde with *trans*-MeOIr(CO)$(PPh_3)_2$ produced $CH_3CH_2OC(O)Me$ in 10 turnovers and MeOC(O)Me in 75% yield after 5 days at room temperature.

Reaction of *trans*-MeOIr(CO)$(PPh_3)_2$ with CH_3CHO. Monitored by ^1H NMR Spectroscopy with Gas Chroma-

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tography. *trans*-$MeOIr(CO)(PPh_3)_2$ (0.025 g, 0.032 mmol) was placed in an NMR tube fitted with a stopcock and placed on a vacuum line. Degassed benzene-d_6 was distilled onto the complex, followed by 0.05 mL of CH_3CHO. The tube was flame sealed, and the reaction was monitored by NMR spectroscopy (after 1 h, 22 h, 2 days, 3 days, and 10 days). The appearance of several products was evident after 22 h. Production of ethyl acetate was obvious [3.86 (q), 1.64 (s) and 0.91 (t) ppm] (with a corresponding decrease in CH_3CHO). Methyl acetate also had assignable peaks [3.38 (s) and 1.65 (s) ppm] as well as the appearance of methanol [3.0 (d) ppm] (detected if the reaction is stopped after 15 min and an NMR spectrum of the distillate is recorded). Small amounts of several other as yet unidentified organic products were also present. Gas chromatographic analysis of the reaction was accomplished by running the reaction in a pressure tube fitted with a side-arm stopcock. The analysis was performed on a Porapak Q column with CH_4 identifiable as a product (this was done against a standard sample containing CH_3CHO).

Preparation of $(MeO)Ir(Me)(I)(CO)(PPh_3)_2$. *trans*-$MeOIr(CO)(PPh_3)_2$[19] (0.25 g) was dissolved in 40 mL of benzene and brought out of the drybox. MeI (0.20 mL), which had been purified by passing down an alumina column, was added to the solution under nitrogen. The reaction was stirred for 5 min, and the solvent was removed in vacuo. The crude solid was purified in the drybox by washing with toluene (2 × 10 mL) and hexanes (2 × 20 mL). The yield was 0.15 g (51%) of a white solid. IR in KBr showed $\nu(CO) = 1985$ cm^{-1}. ^1H NMR in benzene-d_6 showed 1.13 (t, $J_{P-H} = 4.8$ Hz), 3.37 (s), and 7.0 (m) ppm. ^{31}P NMR in benzene-d_6 (^1H NMR decoupled) showed −8.54 (s) ppm. Crystals suitable for crystallographic analysis were grown by slow diffusion of pentane into a saturated solution of the solid in cyclohexane/toluene. Microanal. Calcd: C, 51.03; H, 3.93. Found: C, 50.83; H, 3.93.

Decomposition of $MeOIr(Me)(I)(CO)(PPh_3)_2$. Monitored by IR. $MeOIr(Me)(I)(CO)(PPh_3)_2$ (0.03 g) was suspended in 10 mL of toluene the mixture placed in a pressure tube and brought out of the drybox. An IR spectrum of the cloudy white suspension before the reaction showed 2000 cm^{-1}. The tube was placed in a 45 °C bath and stirred for 1 h. An IR after 1 h of the now yellow suspension showed 2000 (s), 1965 (br, w), and 1730 (w) cm^{-1}. After 4 h the IR showed 2000 (m), 1968 (br, m), and 1730 (m) cm^{-1}. The temperature was raised to 95 °C and the mixture stirred for 5 min. The solution became bright yellow. An IR taken after 20 min at 95 °C showed 1968 cm^{-1} (vs); this was attributed to formation of *trans*-$IIr(CO)(PPh_3)_2$, by comparison to an authentic sample.

Monitored by Gas Chromatography. $MeOIr(Me)(I)(CO)(PPh_3)_2$ (0.03 g) was suspended in 10 mL of toluene and placed in a pressure tube fitted with a side-arm stopcock. The suspension was placed in a 95 °C bath and stirred for 5 min. Gas (500 μL) was removed from the sample with an air-tight syringe and injected into a Varian 2440, Porapak Q column at 60 °C. Methane was detected, but no dimethyl ether was observed.

Monitored by ^1H NMR. $MeOIr(Me)(I)(CO)(PPh_3)_2$ (0.025 g) was placed in an NMR tube fitted with a vacuum adapter. The NMR tube was placed on a vacuum line, and degassed benzene-d_6 was distilled onto the complex (2 drops of C_6H_6 were added initially as a lock). The tube was flame-sealed. A ^1H NMR of the sample in the range of 0–6 ppm showed only 3.4 (s) and 1.13 (t) ppm from $MeOIr(Me)(I)(CO)(PPh_3)_2$ before heating. The tube was placed in a 45 °C bath. After 2 h, the NMR showed a decrease in the starting material peaks, as well as formation of new peaks around 3 ppm. After 4 h the spectrum showed less starting material with a new growth of peaks around 3 ppm. After 7 h a singlet at 3.16 ppm was seen (HCO_2Me) as well as a doublet at 3.0 ppm (MeOH) and starting material. The decomposition after 14 h, 2 days, and 3 days still contained some starting material. After 5 days at 45 °C the starting material had disappeared with the peaks at 3.16 and 3.0 ppm more pronounced. In addition other peaks were also obvious. An unidentified triplet at 1.48 ppm and singlets at 0.33 and 0.17 ppm were also present. The temperature was raised to 75 °C and heated for 14 h. The NMR (now a clear yellow solution) predominately showed peaks around 3 ppm. The doublet at 3.0 ppm corresponded to methanol (approximately 50% based on Ir), and the peak at 3.16 ppm corresponded to methyl formate (approximately 20% based on Ir).

Detection of an Intermediate. $MeOIr(Me)(I)(CO)(PPh_3)_2$ (0.03 g) was suspended in 10 mL of CH_3CN in a pressure tube fitted with a Teflon stopcock. The tube was placed in a 45 °C bath and stirred for 1 h. (The cloudy suspension had turned to a clear solution.) An IR of the solution in CH_3CN showed the decreased intensity of the peak at 1985 cm^{-1} and the appearance of a peak at 1625 cm^{-1}. Removal of the solvent yielded an orange solid which was not stable for long periods of time in solution; however, addition of CH_3CN showed an immediate color change of the solution from orange to yellow (probably indicating an acetonitrile adduct). Attempts to obtain a clean ^1H NMR of the orange solid were not successful, the stability of the solid was short lived, and it was found to revert back to $MeOIr(Me)(I)(CO)(PPh_3)_2$ in solution. The orange compound was presumed to be the five coordinate-carboalkoxy $MeOC(O)Ir(Me)(I)(PPh_3)_2$. Attempts to carbonylate this product directly in order to isolate a stable 18-electron derivative of the complex were attempted.

Carbonylation of the Intermediate. The orange complex (0.03 g) was dissolved in 20 mL of CH_3CN under an inert atmosphere in a Schlenk flask and brought out of the drybox. CO was passed over the solution for 8 h at 45 °C. The resulting product of the carbonylation reaction was found to be $MeOC(O)Ir(Me)(I)(CO)(PPh_3)_2$,[20] based on the IR spectrum of the solid in benzene which showed 2040 (vs) and 1638 (s) cm^{-1} and the ^1H NMR spectrum in benzene-d_6 which showed 7.0 (m), 2.79 (s), and 1.55 (t, $J_{P-H} = 7.5$ Hz) ppm, identical with an authentic sample prepared for comparison.

Carbonylation of $MeOIr(Me)(I)(CO)(PPh_3)_2$. $MeOIr(Me)(I)(CO)(PPh_3)_2$ (0.025 g) was suspended in 20 mL of MeCN and placed in a pressure bottle. The pressure bottle was flushed several times, charged with CO (60 psi), and allowed to stir at room temperature for 2 days. The solvent was removed in vacuo followed by addition of 10 mL of benzene, stirring for 5 min, and evaporation of the benzene to yield a pale yellow solid. An IR spectrum in benzene showed 2040 (vs) and 1638 (s) cm^{-1}. The IR spectrum in KBr showed 2025 (vs) and 1650 (s) cm^{-1}. The ^1H NMR of the solid in benzene-d_6 showed 7.0 (m), 2.79 (s), and 1.55 (t, $J_{P-H} = 7.5$ Hz) ppm. The solid was identified as $MeOC(O)(Ir(Me)(I)(CO)(PPh_3)_2$ based on spectroscopic data and comparison to an authentic sample.[20]

Reaction of $MeOIr(Me)(I)(CO)(PPh_3)_2$ with ^{13}CO. $MeOIr(Me)(I)(CO)(PPh_3)_2$ (0.025 g) was suspended in 20 mL of MeCN and placed in a pressure bottle. The bottle was flushed once, charged with ^{13}CO (60 psi), and allowed to stir at room temperature for 14 h. The solvent was removed in vacuo. Benzene (10 mL) was added to the product, and the solution was stirred for 5 min followed by solvent removal to yield a pale yellow solid. An IR spectrum of the solid in KBr showed 2025 (vs), 1980 (w, shoulder), and 1615 cm^{-1} (s). On the basis of the IR spectrum of the solid, it was estimated that almost total incorporation of the labeled ^{13}CO occurred in the carbomethoxy ligand.

Results and Discussion

Reaction of acid chlorides ($R'C(O)Cl$) with *trans*-$ROIr(CO)(PPh_3)_2$ leads to formation of esters as shown in eq 1. For acetyl chloride and phenylacetyl chloride a second molecule of acid chloride adds to give the six-coordinate iridium complexes. For benzoyl chloride a second molecule does not add and *trans*-$Ir(CO)(PPh_3)_2Cl$ is the only iridium-containing product. The formation of six-coordinate acyl products is a strong indication of a reaction mechanism involving oxidative addition of the acid chloride followed by reductive elimination of the ester $R'C(O)OR$.

Reaction of formaldehyde with the alkoxides *trans*-$ROIr(CO)(PPh_3)_2$ where R = Me, *n*-Pr, *i*-Pr, and *t*-Bu and acetaldehyde with trans-$MeOIr(CO)(PPh_3)_2$ led to two separate paths, one involving formation of C–O bonds

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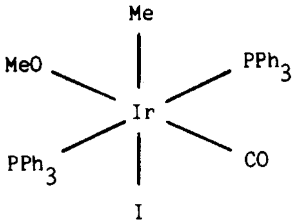

Figure 1. Structure of MeOIr(Me)(I)(CO)(PPh$_3$)$_2$.

R′C(O)OR through a proposed oxidative addition–reductive elimination process and the other involving formation of Tischenko products R′CH$_2$OC(O)R′ (where R′ refers to the aldehyde). These reactions are indicated in eq 2. Again formation of esters occurred upon reaction of the alkoxides with acyl sources. Although the mechanism for the Tischenko reaction has not been fully determined, the fact that *trans*-PhOIr(CO)(PPh$_3$)$_2$ does not react with formaldehyde although NaOPh does, and since *trans*-ClIr(CO)(PPh$_3$)$_2$ and *trans*-MeIr(CO)(PPh$_3$)$_2$ are inactive for the Tischenko reaction suggests that coordination of aldehyde to the iridium center occurs and participation of the alkoxy group depends upon the nucleophilicity of the alkoxy group. This is further demonstrated by the fact that *trans*-PhOIr(CO)(PPh$_3$)$_2$ reacts with CH$_3$COCl to yield PhOC(O)CH$_3$, although no reaction occurs between *trans*-PhOIr(CO)(PPh$_3$)$_2$ and formaldehyde.

In contrast to the reactions of the alkoxide complexes with acyl sources, reaction of the methoxy complex with methyl iodide led to a reasonably stable methyl, methoxy complex. Reaction of *trans*-MeOIr(CO)(PPh$_3$)$_2$ with MeI produced the oxidative addition product MeOIr(Me)(I)(CO)(PPh$_3$)$_2$. The infrared and NMR data are consistent with the six-coordinate, oxidative addition product. The infrared ν(CO) shows a stretch at 1985 cm^{-1}, indicative of an Ir(III) species; the ^{1}H NMR displays a singlet for the methoxy ligand and a triplet for the methyl ligand which couples to the equivalent cis phosphines. In addition ^{31}P NMR (^{1}H decoupled) displays a singlet, again indicative of equivalent phosphines. Microanalysis (C, H) was also in agreement with formation of MeOIr(Me)(I)(CO)(PPh$_3$)$_2$. The structure is as shown in Figure 1.[21]

Since the Me and OMe ligands of MeOIr(Me)(I)(CO)(PPh$_3$)$_2$ were determined to be cis, reductive elimination of dimethyl ether was anticipated. Upon heating (45 °C) the complex slowly begins to decompose; at higher temperatures (90 °C), the complex was found to quickly decompose.

The identifiable products of the decomposition of the alkyl, alkoxy complex were found to be *trans*-IIr(CO)(PPh$_3$)$_2$, CH$_3$OH, CH$_4$, and HCO$_2$Me. No dimethyl ether was detected.

$$\mathrm{MeOIr(Me)(I)(CO)(PPh_3)_2} \xrightarrow{\Delta} \\ trans\text{-}\mathrm{IIr(CO)(PPh_3)_2 + MeOH + CH_4 + HCO_2Me} \quad (3)$$

When the decomposition was performed in coordinating solvents (45 °C) such as acetonitrile, spectroscopic evidence for an intermediate could be seen (IR 1625 cm^{-1}). Carbonylation either of the intermediate or of MeOIr(Me)(I)(CO)(PPh$_3$)$_2$ produces the carbomethoxy complex.

$$\mathrm{MeOIr(Me)(I)(CO)(PPh_3)_2 + CO} \rightarrow \\ \mathrm{MeOC(O)Ir(Me)(I)(CO)(PPh_3)_2} \quad (4)$$

The carbomethoxy product has been previously reported from reaction of MeOC(O)Ir(CO)$_2$(PPh$_3$)$_2$ with methyl iodide.[20] The most probable geometry of this six-coordinate carbomethoxy complex is shown in Figure 2. Thus the carbonylation has occurred with retention of the configuration around iridium as if the external CO directly inserted into the Ir–OMe bond.

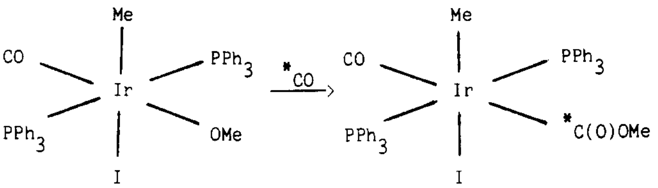

Figure 2. Reaction of MeOIr(Me)(I)(CO)(PPh$_3$)$_2$ with ^{13}CO showing the incorporation of the label into the carbomethoxy group.

Use of ^{13}CO in the carbonylation establishes almost total incorporation of external CO into the carbomethoxy ligand as shown in Figure 2. If an internal methoxide migration occurred, most of the labeled CO would be in the terminal carbonyl of the product. This is not consistent with our observations. It is most likely that the methoxide is displaced by the CO forming a transition-state intermediate of [MeIr(CO)(^{13}CO)(PPh$_3$)$_2$I][OMe]. Iodide dissociation is also possible allowing coordination of ^{13}CO. At this point we favor dissociation of OMe$^-$ because the product would form without isomerization and because the small amount of ^{13}CO incorporation into the terminal carbonyl is consistent with intermolecular OMe$^-$ attack. Further research is necessary to distinguish between OMe$^-$ and I$^-$ dissociation. Such a cation–anion intermediate was previously established for carbonylation of *trans*-ROIr(CO)(PPh$_3$)$_2$.[19,23] The preference for attack on the ^{13}CO arises from the proximity of the OMe$^-$. Attack on ^{12}CO requires that the OMe$^-$ migrate around the octahedron.

The fact that preferential insertion of CO into the Ir–OMe bond occurs, with no evidence for insertion into the Ir–Me bond producing an acyl, is consistent with the carbonylation of (dppe)Pt(OMe)Me).[22]

$$\mathrm{(dppe)Pt(OMe)(Me) + CO \rightarrow (dppe)Pt(CO_2Me)(Me)} \quad (5)$$

On the basis of kinetic studies and NMR experiments, it was concluded that the carbonylation of (dppe)Pt(OMe)(Me) occurs via a five-coordinate carbonyl complex, followed by *internal* insertion of CO.[22] Insertion of CO into the Pt–Me bond to form the acyl was not observed. The carbonylation of MeOIr(Me)(I)(CO)(PPh$_3$)$_2$ leading to the carbomethoxy is interesting since it also shows the preference for insertion into the metal–oxygen bond but cannot occur by an internal insertion. It seems very likely that an ionic mechanism is operative.[19,23]

Formation of ethers from reaction of transition-metal alkoxide complexes with methyl iodide has been previously reported. Reaction of the (dppe)Pt(OMe)(Me) with methyl iodide produced dimethyl ether.[24]

$$\mathrm{(dppe)Pt(OMe)(Me)} \xrightarrow{\mathrm{MeI}} \mathrm{(dppe)Pt(I)(Me) + MeOMe} \quad (6)$$

In addition, reaction of an Fe(II) phenoxide with methyl iodide produced anisole.[25]

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[21] Full Structural details will be reported separately: Fettinger, J. C.; Churchill, M. R.; Private communication.

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$$Fe(OPh)_2(bpy) \xrightarrow{MeI} FeI_2(bpy) + MeOPh \qquad (7)$$

Apparently the energy barrier is lower for formation of the carbomethoxy than it is for reductive elimination of MeOMe in the decomposition of $MeOIr(Me)(I)(CO)(PPh_3)_2$. It is also interesting to note that decomposition of (dppe)Pt(Me)(OMe) did not lead to dimethyl ether but to CH_4 and formaldehyde.[26] For the platinum complex, β elimination through the methoxy ligand, generating a hydrido methyl complex, followed by elimination of methane has been proposed.[26] Apparently β elimination is the favored route since a coordination site is available on the Pt center for abstraction of hydrogen. This is not the case for $MeOIr(Me)(I)(CO)(PPh_3)_2$. The iridium complex is an 18-electron complex, and no evidence for β elimination for the methoxide ligand is found. Although phosphine dissociation could open up a coordination site on the metal, the fact that the complex begins to decompose at relatively low temperatures (45 °C) seems to suggest that this is not occurring.

The formation of esters from the methoxide complex and acid chloride and failure to eliminate MeOMe from the methyl, methoxy complex is very similar to our observations on additions to *trans*-$MeIr(CO)(PPh_3)_2$. Reactions of the methyl complex with acetyl chloride quantitatively produced acetone while reaction of MeI produced a stable dimethyl complex. For the dimethyl complex $Me_2Ir(CO)(PPh_3)_2I$, even extraction of the iodide resulting in $Me_2Ir(CO)(PPh_3)_2^+$ did not result in carbon–carbon bond formation. This indicates that the formation of bonds from these iridium complexes is not the result of a simple explanation such as chloride displacement. We hope that further studies will shed light on the selective formation of bonds.

The formation of methanol and methyl formate as byproducts of the decomposition may have some relevance to the field of CO reduction. The primary products of the homogeneously catalyzed hydrogenation of CO are methanol and methyl formate as well as glycolaldehyde and ethylene glycol.[27] The formation of methanol in these processes has been postulated as occurring via hydroxymethyl ($M–CH_2OH$) intermediates, although recently formation of methanol has been postulated as occurring through metal methoxy intermediates ($M–OCH_3$).[27,28] Similarly, production of methyl formate has been postulated as occurring via metal methoxide intermediates. The formation of glycoaldehyde and ethylene glycol have been proposed as occurring from hydroxy methyl ($M–CH_2OH$) intermediates. In both cases reaction of a hydrogen source with the proposed complexes ($M–OCH_3$ or $M–CH_2OH$) leads to the expected organic products.

The mechanism (shown in Figure 3) suggested for the decomposition of $MeOIr(Me)(I)(CO)(PPh_3)_2$ involves initial formation of a five-coordinate carbomethoxy intermediate. Presumably this intermediate is formed by displacement of the methoxide by a solvent molecule and attack of the methoxide on the coordinated carbonyl. Although we have not done kinetics, we note that this reaction requires warming to 40 °C, in contrast to the carbonylation which proceeds at room temperature. This proposed complex is stabilized in coordinating solvents and can be detected by infrared. We cannot rule out formation of this complex as a result of a prior isomerization of $MeOIr(Me)(I)(CO)(PPh_3)_2$, in which the OMe and CO ligands orient in a cis fashion favorable for nucleophilic attack of OMe onto CO as opposed to formation of a cation–anion type intermediate in which the OMe group enters the outer coordination sphere of the complex. Precedence exists for both although facile isomerization of six-coordinate iridium(III) is only observed when at least one ligand is a hydride.[29] The labeling in the carbonylation reaction shows that in this case the cation–anion mechanism is operative. The fact that the OMe ligand is a relatively strong nucleophile has been shown in the carbonylation of *trans*-$MeOIr(CO)(PPh_3)_2$.[19,23] The final step of the proposed mechanism involves a hydrogen source (undetermined as yet) which can enter the coordination sphere and form methanol, methyl formate, and methane.

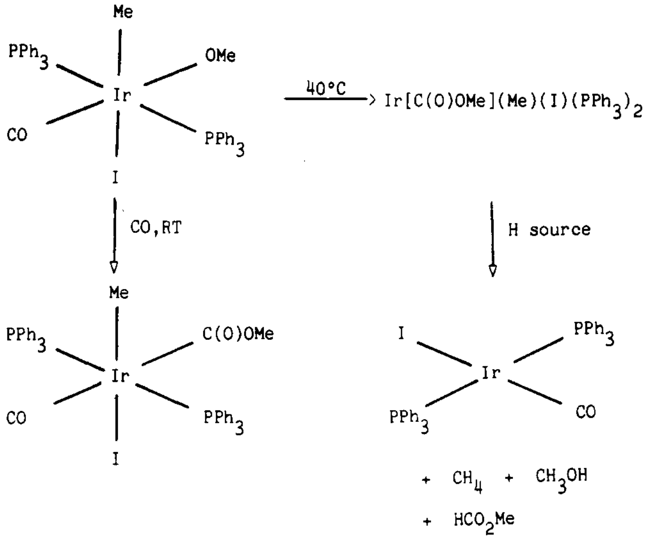

Figure 3. Suggested scheme for the decomposition of $MeOIr(Me)(I)(CO)(PPh_3)_2$.

The reactions reported in this paper involving *trans*-$ROIr(CO)(PPh_3)_2$ with aldehydes, acid chlorides, and methyl iodide show that formation of carbon–oxygen bonds depends on the specific group. Combination of alkoxy and acyl groups (whether from aldehydes or acid chlorides) occurs very readily. Elimination of ester from a transition-metal complex through a C–O bond-forming reaction has been a postulated step in aldehyde reduction as well as CO reduction based upon the generation of formate esters in these processes. In contrast, reaction of methyl iodide does not result in elimination of an ether. The elimination of esters upon reaction of the iridium alkoxide complexes with acyl sources and lack of elimination of ethers upon interaction with alkyl sources indicate that C–O bond formation has features similar to C–C bond-forming reactions where elimination of two alkyls to give alkanes is much less favorable than elimination of ketone from a complex containing an alkyl and an acyl.[30]

Acknowledgment. We acknowledge the National Science Foundation (CHE-8709563) for support of this research and Jeff Thompson for help with microanalysis.

Registry No. *trans*-$MeOIr(CO)(PPh_3)_2$, 94070-38-9; $CH_3C(O)IrCl_2(CO)(PPh_3)_2$, 33394-10-4; $HIrCl_2(CO)(PPh_3)_2$, 17000-10-1; *trans*-$PhOIr(CO)(PPh_3)_2$, 94070-40-3; $PhOC(O)CH_3$, 122-79-2;

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trans-$ClIr(CO)(PPh_3)_2$, 15318-31-7; $PhC(O)OMe$, 93-58-3; $PhCH_2C(O)IrCl_2(CO)(PPh_3)_2$, 33395-39-0; $PhCH_2C(O)OMe$, 101-41-7; *trans-n*-$PrOIr(CO)(PPh_3)_2$, 94070-39-0; *trans-i*-$PrOIr(CO)(PPh_3)_2$, 99688-37-6; *trans-t*-$BuOIr(CO)(PPh_3)_2$, 98720-65-1; CH_3CHO, 75-07-0; $CH_3CH_2OC(O)Me$, 141-78-6; $MeOIr(Me)(I)(CO)(PPh_3)_2$, 107799-54-2; *trans*-$IIr(CO)(PPh_3)_2$, 19472-16-3; $MeOC(O)Ir(Me)(I)(PPh_3)_2$, 118515-37-0; $MeOC(O)Ir(Me)(I)(CO)(PPh_3)_2$, 118626-13-4; acetyl chloride, 75-36-5; methyl acetate, 79-20-9; benzoyl chloride, 7631-42-7; phenylacetyl chloride, 103-80-0; paraformaldehyde, 30525-89-4; methyl formate, 107-31-3; *n*-propyl formate, 110-74-7; *tert*-butyl formate, 762-75-4; *i*-propyl formate, 625-55-8; methanol, 67-56-1.

Reactions of $(\eta^5\text{-}C_5R_5)Co(C_2H_4)_2$ (R = H, Me) with Selected 1,2,3-Selenadiazoles

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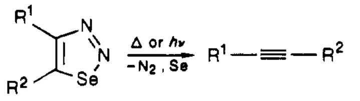
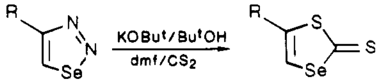
The reactions of $(\eta^5\text{-}C_5R_5)Co(C_2H_4)_2$ (R = H, Me) with cycloocta-1,2,3-selenadiazole and more saturated analogues have been studied. Products of three types have been isolated and characterized. The reactions of $(\eta^5\text{-}C_5H_5)Co(C_2H_4)_2$ yield binuclear complexes $[(\eta^5\text{-}C_5H_5)Co]_2(\mu_2\text{-}\eta^3,\eta^2\text{-}C_8H_xSe)$ (x = 6, 10, 12) which are fluxional in solution. The reactions of $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)_2$ yield mononuclear complexes. Those derived from the less saturated 1,2,3-selenadiazoles are of the form $(\eta^5\text{-}C_5Me_5)Co(\eta^4\text{-}C_8H_x(Se)CHCH_3)$ (x = 6, 8), in which a molecule of ethene has been incorporated into the organoselenium ligand. Those derived from the more saturated 1,2,3-selenadiazoles, $(\eta^5\text{-}C_5Me_5)Co(\eta^2\text{-}C_8H_xSe)(\eta^1\text{-}C_8H_xSeN_2)$ (x = 10, 12), contain an intact 1,2,3-selenadiazole ligand. ^1H and ^{13}C NMR spectroscopy in particular have been used to probe the structures of these compounds.

Introduction

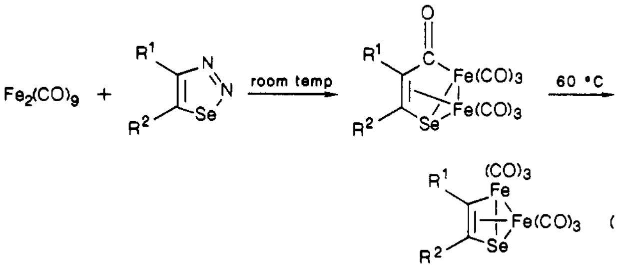
Interest in 1,2,3-selenadiazoles over the last 20 years has centered on their utility in organic synthesis.[1] The chemistry of 1,2,3-selenadiazoles is dominated by the facility with which dinitrogen is eliminated: the fate of the residual organoselenium fragment determines the outcome of the reaction. When selenium is readily lost from this fragment, 1,2,3-selenadiazoles serve as intermediates in the preparation of alkynes (eq 1). A number of strained cycloalkynes, inaccessible by other routes, have been prepared in this way.[2-4] When selenium is retained, a variety of products may be formed (see Scheme I[5]). In the presence of external reagents the selenium-containing intermediates can be trapped to yield addition products (e.g. eq 2[6]).



(1)

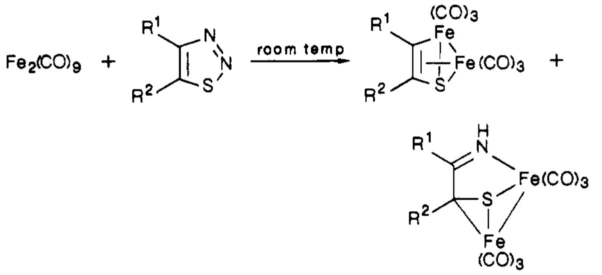


(2)



(3)

We are interested in the ability of 1,2,3-selenadiazoles to function as ligands or ligand precursors in transition-metal complexes. Comparatively little work has been done in this area. A number of research groups have studied the reaction of nonacarbonyldiiron with 1,2,3-selenadiazoles (eq 3).[7] Interestingly, a different type of product was isolated from analogous reactions with 1,2,3-thiadiazoles (eq 4).[8] The preparation of 1,2,3-thiadiazole and 1,2,3-selenadiazole pentacarbonyl complexes of the ele-



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