from the indenyl plane. The distance C3–C3′ [160.2 (1.4) pm] is significantly longer than the "normal" C–C bond length between sp^3-hybridized carbon atoms. It is comparable, however, to what has been found in the bis(azulenyl) complexes [6-Mn(CO)$_3$]$_2$ and [6-Mo(Me)(CO)$_3$]$_2$ (158 pm).[12]

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Registry No. 1, 14024-00-1; (*pR,R*)-**2a**, 111349-33-8; (*pR,S*)-**2a**, 111464-95-0; (*pR,R*)-**2b**, 111349-34-9; (*pR,S*)-**2b**, 111465-82-8; **3a**, 111349-36-1; **3b**, 111349-38-3; **5a**, 111464-96-1; **5b**, 111349-39-4; C_5H_5Me, 26519-91-5; *s*-BuBr, 78-76-2; 1,2-C_5H_4(Me)-*s*-Bu, 111324-78-8; 1,3-C_5H_4(Me)-*s*-Bu, 111378-83-7.

Supplementary Material Available: Listings of refined atomic coordinates and anisotropic temperature factors, bond lengths, bond angles, and best planes and a numbering scheme (8 pages); a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

Evidence for C–O Bond Formation, Aldehyde Decarbonylation, and Dimerization by Reaction of Formaldehyde and Acetaldehyde with *trans*-ROIr(CO)(PPh$_3$)$_2$

Karen A. Bernard and Jim D. Atwood*

Department of Chemistry, University at Buffalo
State University of New York
Buffalo, New York 14214

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Summary: The reaction of formaldehyde and acetaldehyde with *trans*-ROIr(CO)(PPh$_3$)$_2$ (R = Me, *i*-Pr, *n*-Pr, *t*-Bu) leads to formation of esters ROC(O)R′ (R′ = H or Me) by formation of a carbon–oxygen bond between the alkoxide and the acyl from the aldehyde and to catalytic production of the ester R′CH$_2$C(O)OR′ in a Tischenko reaction.

Reactions of aldehydes form the basis for many organic syntheses.[1] Reactions of aldehydes with metal complexes have been observed with a range of products formed.[2–10] Aldehydes react with metal bases in aldol condensation reactions, with strong bases in Cannizzaro reactions, and with aluminum alkoxides in Tischenko reactions.[11,12] The Tischenko reaction is an interesting dimerization that occurs by disproportionation of the aldehyde

$$2RC(O)H \xrightarrow{cat.} RCH_2OC(O)R$$

and may formally be considered as addition of a C–H bond to the carbon–oxygen double bond. This reaction is most effectively catalyzed by aluminum alkoxides[11–13] but can also be effected by transition-metal complexes.[14,15] As part of our continuing investigation of the interaction of organic molecules with *trans*-ROIr(CO)(PPh$_3$)$_2$,[16–23] we now communicate our preliminary observations on the reactions of formaldehyde and acetaldehyde with iridium alkoxides. These reactions lead to two separate paths, one involving Tischenko reactions and the other involving oxidative addition of the C–H bond to the iridium.

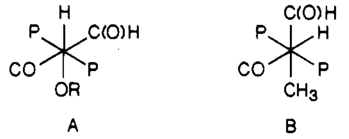
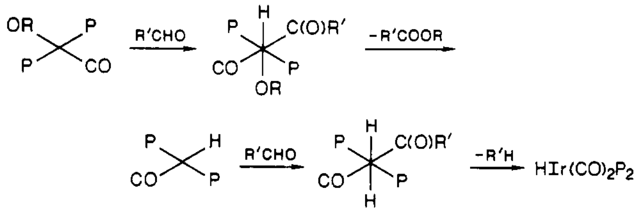


Figure 1. Suggested geometries for the formaldehyde oxidative addition to *trans*-ROIr(CO)(PPh$_3$)$_2$ (A) and *trans*-MeIr(CO)(PPh$_3$)$_2$ (B).

Scheme I[a]



[a] Abbreviations: P = PPh$_3$; R = Me, *n*-Pr, *i*-Pr, *t*-Bu; R′ = H, Me. The scheme is suggested for carbon–oxygen bond formation in reaction of aldehydes with *trans*-ROIr(CO)(PPh$_3$)$_2$. We cannot, at this time, rule out initial insertion of aldehyde into the Ir–OR bond followed by β-elimination.

Reactions of *trans*-ROIr(CO)(PPh$_3$)$_2$ (R = Me, *i*-Pr, *n*-Pr, or *t*-Bu)[24] with CH_2O and of *trans*-ROIr(CO)(PPh$_3$)$_2$ (R = Me) with CH_3CHO lead to catalytic production of Tischenko products, R′CH$_2$OC(O)R′, and to production of oxidative-addition, reductive-elimination products, R′C(O)OR, where R′ = Me or H, at ambient conditions over a period of several days.[25] When reaction ceases, the

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[24] Prepared as previously described.[17,18]

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only observable iridium product is $HIr(CO)_2(PPh_3)_2$.[26] Attempted reaction of formaldehyde with *trans*-$PhOIr(CO)(PPh_3)_2$, *trans*-$C_6F_5OIr(CO)(PPh_3)_2$, *trans*-$Ir(CO)(PPh_3)_2Cl$, and *trans*-$MeIr(CO)(PPh_3)_2$ have provided no evidence for Tischenko products or C–O, C–Cl, or C–C bond formation.

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. These reactions have been accomplished for R = Me, *n*-Pr, and *t*-Bu. There was no evidence for other products or intermediates. 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. In addition an intermediate (IR: 2018 and 1668 cm^{-1}), which is probably the product of oxidative addition of a C–H bond of acetaldehyde, and small amounts of CH_3OH and CH_4 were observed.

The two reactions (C–O bond formation and Tischenko) observed upon interaction of formaldehyde (and acetaldehyde) with *trans*-$ROIr(CO)(PPh_3)_2$ appear to occur by separate mechanisms with C–O bond formation possibly a termination step for the catalytic reaction. Scheme I describes the suggested steps for $ROC(O)R'$ formation that involve oxidative addition of a C–H bond of the aldehyde, reductive elimination of $ROC(O)R'$, and oxidative addition and decarbonylation of a second aldehyde. Such decarbonylation reactions are well-established. The elimination of ester by C–O bond formation is consistent with the observations on acid chloride reactions with the methoxy complex[21] but in contrast to the reaction of $H_2C(O)$ with *trans*-$CH_3Ir(CO)(PPh_3)_2$ which leads only to CH_4 and $HIr(CO)_2(PPh_3)_2$.[27] This difference may result from the geometry of the formed six-coordinate oxidative-addition product. Addition of $H_2C(O)$ to *trans*-$CH_3Ir(CO)(PPh_3)_2$ probably leads to the geometry where the strong donor CH_3 and H are not trans while addition of aldehyde to *trans*-$ROIr(CO)(PPh_3)_2$ should lead to a geometry with the strong donor H trans to the weak donor OR. The suggested geometries are shown in Figure 1. Thus the different reductive elimination products may result from different stereochemistries. We and others have previously demonstrated that stereochemistry may provide selectivities in reductive elimination reactions.[28-31]

The mechanism for formation of Tischenko products is not fully determined at this point, but the following must be accommodated: (1) Tischenko products are observed for the reactions of *trans*-$ROIr(CO)(PPh_3)_2$ (R = Me, *i*-Pr, *t*-Bu, *n*-Pr) with formaldehyde and for the reaction of *trans*-$ROIr(CO)(PPh_3)_2$ (R = Me) with CH_3CHO but not for the reaction of *trans*-$ROIr(CO)(PPh_3)_3$ (R = Ph or C_6F_5) with formaldehyde. (2) The reaction proceeds similarly in C_6H_{12}, C_6H_6, and THF. (3) The hydride, $HIr(CO)(PPh_3)_2$, does not appear to be the active catalyst. Attempts to generate this hydride by heating $HIr(CO)(PPh_3)_3$ and by allowing elimination of CH_4 from $CH_3Ir(H_2)(CO)(PPh_3)_2$ in the presence of aldehyde produced no Tischenko products. (4) *trans*-$Ir(CO)(PPh_3)_2Cl$ and *trans*-$CH_3Ir(CO)(PPh_3)_2$ are inactive for the Tischenko reaction. (5) NaOPh reacts with formaldehyde to give phenyl formate while reaction of *trans*-$PhOIr(CO)(PPh_3)_2$ with formaldehyde gives no reaction. Evidently free phenoxide is not present. Since *trans*-$PhOIr(CO)(PPh_3)_2$ reacts with acid chlorides to give esters,[32] the failure to react with formaldehyde suggests that the C–H bonds are not sufficiently activated for reaction and that a specific coordination is required both for C–O bond formation and for Tischenko products.

These data suggest a coordination of the aldehyde to the iridium and participation of the alkoxy group that depends on the nucleophilicity of the alkoxy group. Further studies will be necessary to more fully describe the mechanism of catalytic formation of Tischenko products by *trans*-$ROIr(CO)(PPh_3)_2$.

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Registry No. $HIr(CO)_2(PPh_3)_2$, 17250-59-8; *trans*-$MeOIr(CO)(PPh_3)_2$, 94070-38-9; *trans*-*n*-$PrOIr(CO)(PPh_3)_2$, 94070-39-0; *trans*-*i*-$PrOIr(CO)(PPh_3)_2$, 99688-37-6; *trans*-*t*-$BuOR(CO)(PPh_3)_2$, 98720-65-1; HC(O)OMe, 107-31-3; HC(O)OPr-*i*, 625-55-8; HC(O)OPr-*n*, 110-74-7; HC(O)OBu-*t*, 762-75-4; $CH_3C(O)OEt$, 141-78-6; $H_2C(O)$, 50-00-0; CH_3CHO, 75-07-0.

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[25] (a) **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 stirred. The reaction was monitored by IR. The appearance of a peak at 1727 cm^{-1} (methyl formate) occurred within $^1/_2$ h of reaction and continued to grow. The IR 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 (1 week). Further confirmation of methyl formate as the byproduct of the reaction was accomplished by analysis of the reaction distillate through ^1H NMR and gas chromatography. Gas chromatography was performed by using a Varian 2440 FID, Carbowax 20M column at 60 °C. The solvent 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 found to be $HIr(CO)_2(PPh_3)_2$: IR (C_6H_{12}) showed 2085 (m, br), 1993 (s), 1983 (m), 1945 (vs), 1935 (s) cm^{-1}. (b) The reactions with *n*-$PrOIr(CO)(PPh_3)_2$, *i*-$PrOIr(CO)(PPh_3)_2$, and *t*-$BuOIr(CO)(PPh_3)_2$ were accomplished under similar conditions. The reaction of *trans*-*n*-$PrOIr(CO)(PPh_3)_2 + H_2C(O)$ was also examined by NMR. The organic products were found to be methyl formate, as well as *n*-propyl formate by comparison to authentic samples. The reaction of *trans*-*t*-$BuOIr(CO)(PPh_3)_2 + H_2CO$ was also examined by NMR. The organic products were found to be *t*-butyl formate, as well as methyl formate. (c) The reaction of *trans*-$PhOIr(CO)(PPh_3)_2$ with $H_2C(O)$ was attempted under similar conditions. No reaction was evident after 3 days. (d) **Reaction of *trans*-$MeOIr(CO)(PPh_3)_2$ with CH_3CHO.** 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. After 3 h the IR showed 2018 (s), 1958 (vs), and 1668 (m) in addition to 1730 (vs, br) (CH_3CHO). 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 showed the formation of $HIr(CO)_2(PPh_3)_2$ as well as the peak at 1958 cm^{-1}. The presumed oxidative addition product (2018, 1668 cm^{-1}) had disappeared for the most part. (e) **Reaction of *trans*-$MeOIr(CO)(PPh_3)_2$ with CH_3CHO Monitored by NMR.** *trans*-$MeOIr(CO)(PPh_3)_2$ (0.25 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 (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 (with a corresponding decrease in acetaldehyde). Methyl acetate also had assignable peaks, as well as the appearance of methanol (detected if the reaction is stopped after 15 min and an NMR of the distillate recorded). Small amounts of several other as yet unidentified organic products were also present. (f) Gas chromatography of the reaction was accomplished by running the reaction in a pressure tube fitted with a 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).

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