Acetalization and Transacetalization Reactions Catalyzed by Ruthenium, Rhodium, and Iridium Complexes with {2-{{Bis[3-(trifluoromethyl)phenyl]phosphino}methyl}-2-methylpropane-1,3-diyl}bis[bis[3-(trifluoromethyl)phenyl]phosphine] ($MeC[CH_2P(m\text{-}CF_3C_6H_4)_2]_3$)

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The complexes $[RhCl_{(3-n)}(MeCN)_n(CF_3triphos)](CF_3SO_3)_n$ ($n = 1$, 2; $CF_3triphos = MeC[CH_2P(m\text{-}CF_3C_6H_4)_2]_3$) and $[M(MeCN)_3(CF_3triphos)](CF_3SO_3)_n$ ($M = Ru$, $n = 2$; $M = Ir$, $n = 3$) are catalyst precursors for some typical acetalization and transacetalization reactions. The activity of these complexes is higher than those of the corresponding species containing the parent ligand $MeC[CH_2P(C_6H_5)_2]_3$(Htriphos). Also the complexes $[MCl_3(tripod)]$ (tripod = Htriphos and CF_3triphos) are active catalysts for the above reactions. The complex $[RhCl_2(MeCN)(CF_3triphos)](CF_3SO_3)$ catalyzes the acetalization of benzophenone.

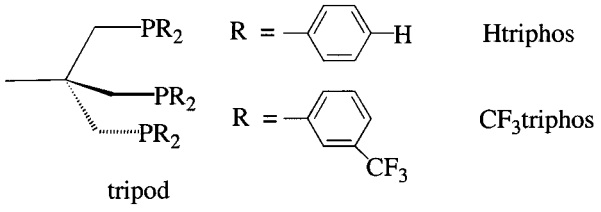
1. Introduction. – The carbonyl group of aldehydes and ketones is probably the most versatile function in organic chemistry, and much effort has been expended on protection of carbonyls, usually in the form of acetals [1][2]. These derivatives are most commonly prepared by reacting the carbonyl compounds with the appropriate alcohols in the presence of a *Lewis* acid, usually protonic acids [1–3].

Some transition-metal complexes also catalyze the formation of acetals, *e.g.* $[RhCl(PPh_3)_3]$ [4], $[Rh_2Cl_2(CO)_4]$ [5], $[RuCl_2(PPh_3)_3]$ [6], $[RhH(CO)(PPh_3)_3]$ [7], $[RuHCl(PPh_3)_3]$ [8], and $[Rh(nbd)(Ph_2P(CH_2)_4PPh_2)](ClO_4)$ (nbd = norbornadiene) [9]; their activities were discovered accidentally.

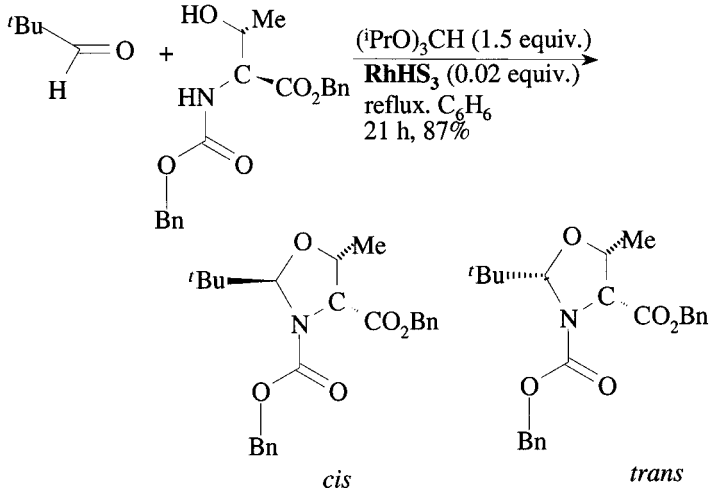
More recently, the complexes $[M(H_2O)_2(Ph_2PCH_2CH_2PPh_2)](CF_3SO_3)_2$ (M = Pd, Pt) [10], $[RhCl_{(3-n)}(MeCN)_n(Htriphos)](CF_3SO_3)_n$ ($n = 1$, 2, 3; **RhHS**$_n$) [11][12], $[Ru(MeCN)_3(Htriphos)](CF_3SO_3)_2$ (**RuHS**$_3$) [13][14], and $[Ru(MeCN)_3\{PhP(CH_2CH_2PPh_2)_2\}](CF_3SO_3)_2$ [15] were shown to be excellent catalyst precursors for acetalization and transacetalization reactions (**H** = Htriphos = {2-[(diphenylphosphino)methyl]-2-methylpropane-1,3-diyl}bis[diphenylphosphine]; **S** = solvent). These complexes are particularly useful for the acetalization of acid-sensitive carbonyl compounds [10–12]. Furthermore, **RuHS$_3$** proved to be an efficient catalyst for the formation of dioxanyl- and dioxolanylphenols [13] as well as the deprotection of acetals and tetrahydropyranylphenols [14]. One of the more interesting reactions, readily catalyzed by the Htriphos-containing complexes [16], is that shown in *Scheme 1*. While these complexes show useful reactivities, they do not catalyze the acetalization of diaryl ketones [17].

Olah and co-workers [18] reported that benzophenone dimethyl acetal is formed when the diaryl ketone benzophenone is treated with trimethyl orthoformate

[1]) Deceased October 11, 2000.



Scheme 1



in the presence of *Nafion-H*®; however this reaction could still be improved, as shown below.

Recent studies have shown that complexes of type $[M(MeCN)_3(tripod)](CF_3SO_3)_n$ (M = Ru, $n = 2$, **RuFS$_3$** [19]; M = Rh, $n = 3$, **RhFS$_3$** [20]; M = Ir, $n = 3$, **IrFS$_3$** [19]), containing the tripodal phosphine $MeC[CH_2P(m\text{-}CF_3C_6H_4)_2]_3$ (CF_3triphos = **F** = {2-{{bis[3-(trifluoromethyl)phenyl]phosphino}methyl}-2-methylpropane-1,3-diyl}bis-[bis[3-{trifluoromethyl)phenyl]phosphine]) [20], are stronger *Lewis* acids than the corresponding compounds containing Htriphos, *i.e.* **RuHS$_3$**, **RhHS$_3$**, and **IrHS$_3$**, respectively [12][19][21][22]. Therefore, the activities of the complexes $[RhCl_{(3-n)}(MeCN)_n(CF_3triphos)](CF_3SO_3)_n$ ($n = 1, 2$) and $[M^{(z+)}(MeCN)_3(CF_3\text{-}triphos)](CF_3SO_3)_z$ ($M = Ru^{2+}$, Rh^{3+}, Ir^{3+}) as catalysts for the acetalization and transacetalization reactions were investigated. For comparison purposes, the activities of the corresponding Htriphos species were also studied.

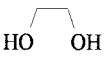
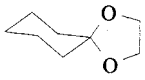
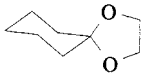
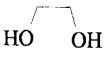
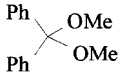
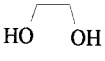
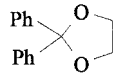
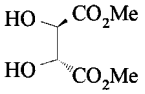
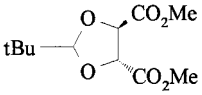
2. Results. – *2.1 Catalyst Precursors.* The catalyst precursors tested in this study were: $[RhCl_2(MeCN)(tripod)](CF_3SO_3)$ (tripod = CF_3triphos, **RhFS$_1$** [20]; tripod = Htriphos, **RhHS$_1$** [12][22], $[RhCl(MeCN)_2(tripod)](CF_3SO_3)_2$ (tripod = CF_3triphos, **RhFS$_2$** [20]; tripod = Htriphos, **RhHS$_2$** [12][22]), $[M(MeCN)_3(tripod)](CF_3SO_3)_3$ (M = Rh, tripod = CF_3triphos, **RhFS$_3$** [20]; M = Rh, tripod = Htriphos; **RhHS$_3$** [12][22]; M = Ir, tripod = CF_3triphos, **IrFS$_3$** [19]; M = Ir, tripod = Htriphos; **IrHS$_3$**

[19]), $[Ru(MeCN)_3(tripod)](CF_3SO_3)_2$ (tripod = CF_3triphos, **$RuFS_3$** [19]; tripod = Htriphos, **$RuHS_3$** [21]), $[RhCl_3(tripod)]$ (tripod = CF_3triphos, **$RhFCl_3$** [20]; tripod = Htriphos, **$RhHCl_3$** [23][24]), and $[IrCl_3(tripod)]$ (tripod = CF_3triphos, **$IrFCl_3$** [19]; tripod = Htriphos, **$IrHCl_3$** [19][23][25][26]).

2.2. *Investigated Acetalization Reactions.* The reactions tested and the reaction conditions used in this study were similar to those reported in previous publications from this laboratory [10–15]. Some of these reactions, with **$RhFS_1$** as catalyst precursor, are listed in the *Table*.

It has been found that the complexes containing CF_3triphos are at least as active as those containing Htriphos [27]. However, Htriphos is commercially available [28], and the preparation of CF_3triphos is not trivial [20]. Thus, a comparative study of the activities of corresponding complexes of the two ligands was carried out to determine the cases in which the use of complexes containing CF_3triphos is essential or particularly advantageous.

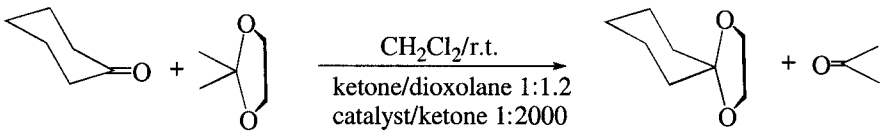
Table. *Some Acetalization Reactions Catalyzed by [$RhCl_2$(MeCN)(CF_3triphos)](CF_3SO_3)(*$RhFS_1$*)*

Carbonyl compound	Alcohol	Reagent ratio	Temp., time	Drying agent	Product	Yield [%]
		1 : 1.05	r.t., 3 h	IOF[a])		80[b])
		1 : 1.1	r.t., 5 min	none		89[b])
		1 : 1	r.t., 20 min	none		83[b])
	MeOH	1 : 5	r.t., 5 d	MOF[c])		80[d])
		1 : 1.3	reflux[e]), 41 h	AD[f])		56[b])
		1 : 0.6	r.t., 24 h	IOF[a])		100[b])

[a]) IOF = Isopropyl orthoformate. [b]) Yield determined by GC, with mesitylene as internal standard. [c]) MOF = Methyl orthoformate. [d]) Isolated yield. [e]) Reflux temperature. [f]) Azeotropic distillation.

2.3. *Comparison of the Rates of Acetalization*. The standard reaction chosen for this purpose was that of cyclohexanone with 2,2-dimethyl-1,3-dioxolane (*Scheme 2*). The rate of the reaction with **$RhFS_1$** was more that 100 times higher than that with **$RhHS_1$** (see *Fig. 1*). Rate enhancements were observed also for **$IrFS_3$** relative to **$IrHS_3$** (see *Fig. 2*).

Scheme 2



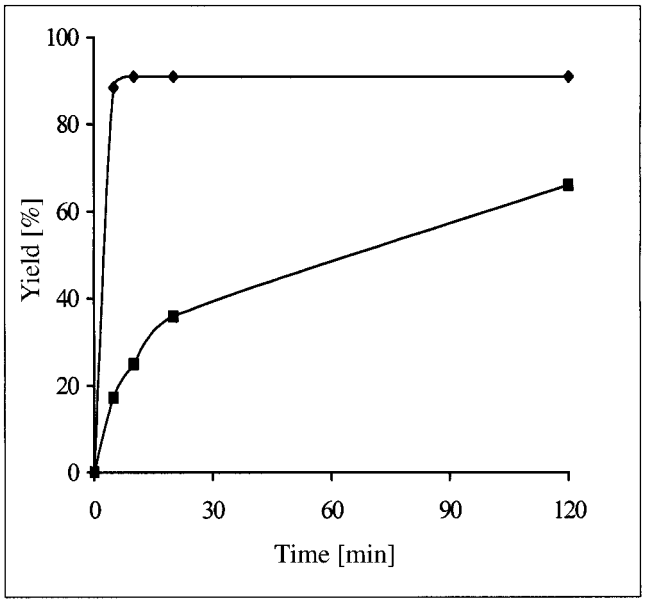


Fig. 1. *Transacetalization reaction of cyclohexanone with 2,2-dimethyl-1,3-dioxolane* (*Scheme 2*) *at room temperature with* **$RhFS_1$** (◆) *and* **$RhHS_1$** (■) *as catalyst precursors*

As **$RhHS_3$**, **$RuFS_3$**, and **$RuHS_3$** give comparable rates at room temperature (see *Fig. 2*), measurements were also carried out at 0°. At this temperature, the rate observed in the presence of **$RuFS_3$** was twice that of **$RuHS_3$** (see *Fig. 3*). The rates for **$IrFS_3$** and **$IrHS_3$** were very slow (not shown).

2.4. *Relative Activities of Rhodium(III), Iridium(III), and Ruthenium(II)*. The reaction shown in *Scheme 2* was also used to compare the reactivities of the different metal centers. Thus, at room temperature, this reaction was complete within 5 min in the presence of **$RuFS_3$** and **$RhFS_3$**, while with **$IrFS_3$**, it took *ca.* 30 min (see *Fig. 2*). In all cases, the yields ranged from 80 to 85%. It should be noted that **$RhFS_3$** decomposed within a few min after addition to the reaction mixture. As this did not affect the product yield, either the formation of the acetal was faster than the decomposition of

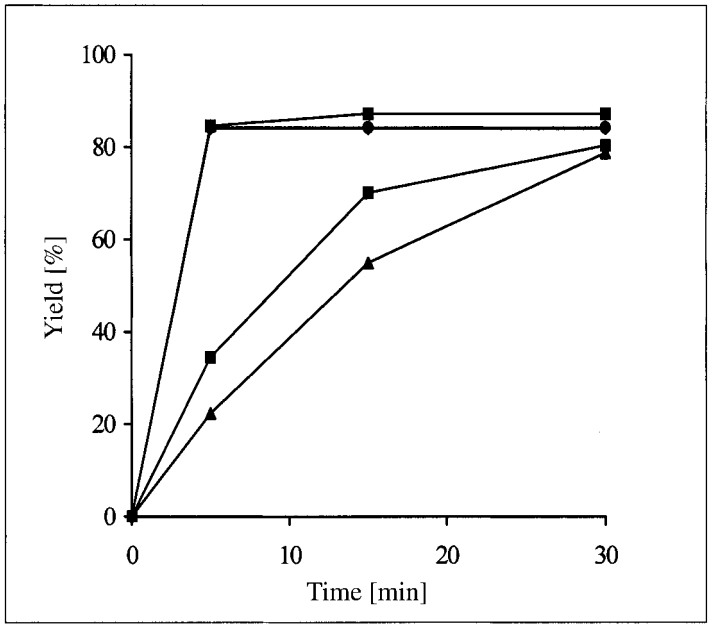


Fig. 2. *Transacetalization reaction of cyclohexanone with 2,2-dimethyl-1,3-dioxolane* (*Scheme 2*) *at room temperature with* **$RuFS_3$** (●), **$RuHS_3$** (■, upper), **$RhHS_3$** (◆, superimposed on ●), **$IrFS_3$** (■, lower) *and* **$IrHS_3$** (▲) *as catalyst precursors*

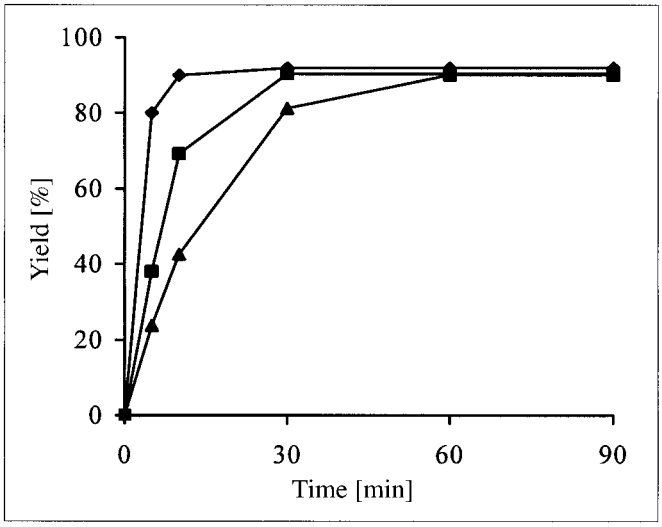
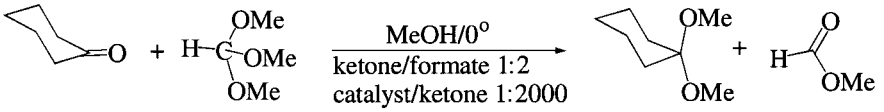


Fig. 3. *Transacetalization reaction of cyclohexanone with 2,2-dimethyl-1,3-dioxolane* (*Scheme 2*) *at 0° with* **$RuFS_3$** (■), **$RuHS_3$** (▲), *and* **$RhHS_3$** (◆) *as catalyst precursors*

catalyst or its decomposition product(s) also catalyzed this reaction. Thus, the order of the reactivity of the complexes is $\mathbf{RhFS_3} > \mathbf{RuFS_3} > \mathbf{IrFS_3}$.

2.5. *Catalytic Activities of the Trichloro Complexes.* Uncharged trichlororhodium and trichloroiridium complexes [$RhCl_3(CF_3$triphos)] (**$RhFCl_3$**) [20], [$RhCl_3$(Htriphos)] (**$RhHCl_3$**) [23][24], [$IrCl_3(CF_3$triphos)] (**$IrFCl_3$**) [19], and [$IrCl_3$(Htriphos)] (**$IrHCl_3$**) [19][23][25][26] were also tested as catalyst precursors for the acetalization of cyclohexanone with MeOH in the presence of methyl orthoformate (*Scheme 3*). As can be seen from *Fig. 4*, these complexes efficiently catalyzed the reaction in *Scheme 3*. Interestingly, in the case of these precursors, the CF_3triphos complexes gave the lower reaction rates.

Scheme 3



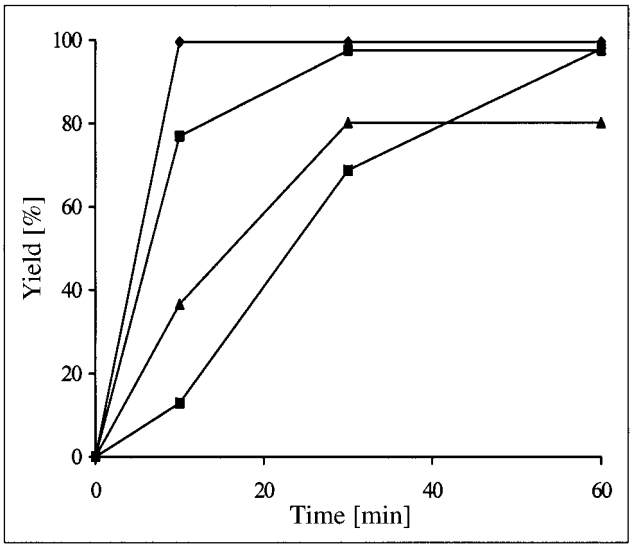
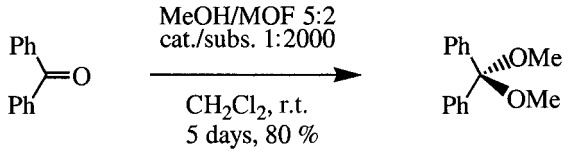


Fig. 4. *Acetalization reaction of cyclohexanone with methyl orthoformate* (*Scheme 3*) *at 0° with* **$RhFCl_3$** (■, upper), **$RhHCl_3$** (◆), **$IrFCl_3$** (■, lower) *and* **$IrHCl_3$** (▲) *as catalyst precursors*

2.6. *Acetalization of Benzophenone.* Benzophenone was acetalized to $Ph_2C(OMe)_2$ by MeOH and $HC(OMe)_3$ in CH_2Cl_2, in the presence of [$RhCl_2$(MeCN)(CF_3triphos)](CF_3SO_3) (**$RhFS_1$**) (*Scheme 4*). The reaction did not require special conditions: reagents and catalyst precursor were stirred in CH_2Cl_2 at room temperature, albeit for 5 days. The reaction was only slightly faster in toluene at 60°, requiring 4 days to go to completion.

Benzophenone reacted also with ethylene glycol, in the presence of isopropyl orthoformate and the complex **$RhFS_1$** as catalyst precursor (see *Table*), to give the

Scheme 4



corresponding acetal in 56% yield. This yield was not improved on addition of a second aliquot of catalyst precursor after the reaction had stopped.

3. Discussion. – 3.1. *Relative Reactivities of Corresponding Complexes of CF_3triphos* vs. *Htriphos*. The reactivity differences caused by the replacement of Htriphos by CF_3triphos (see *Figs. 1–3*) is related to differences in the degree of electron donation.

As pointed out earlier, the electron-donor capacity of CF_3triphos is lower than that of Htriphos. It follows that the effective nuclear charge, at any given metal center, will be higher in the corresponding complex with the former ligand. The observation that, *in the cationic complex*, the overall rates are faster for the CF_3triphos-containing compounds than for their Htriphos analogs indicates that changes in ligand exchange rates *do not* determine the observed reactivity differences. The difference in electron distribution in the coordinated C–O bond of the carbonyl compound is likely to be responsible for the observed differences.

3.2. *Relative Reactivities of the Three Metal Centers*. The observed differences in reactivity can also be attributed to the different effective nuclear charges of the three metal centers. Thus, with each ligand, the effective nuclear charge at the ruthenium atom of **$RuFS_3$** is expected to be lower than that at the rhodium atom of **$RhFS_3$**, mainly because the oxidation state of the metal atom in the former is II while that of the latter is III [29].

On the other hand, the Rh^{III}–O bond is likely to be stronger than the corresponding Ru^{II}–O bond because the ionic charge at the former metal center is higher than that at the latter; moreover, these M–O bonds have a large 'ionic' component. Thus, the partial positive charge at the C-atom of the ketone is likely to be higher in the rhodium than in the ruthenium complex. This will result in a faster rate of the nucleophilic attack in **$RhFS_3$** than in **$RuFS_3$**. As this step appears to determine the overall rate of reaction in these complexes (see above), the former complex should give the faster reaction, as observed.

The slower acetalization rate shown by the iridium complexes is most likely due to a change in nature of the rate-determining step in the overall reaction, *i.e.*, from nucleophilic attack to ligand exchange. This follows from the general observation that the effective nuclear charge at a given metal center of the third transition-metal series is higher than at the corresponding center of the second transition series [31]. Thus, if, as proposed for **$RhFS_3$**, the rate-determining step is a nucleophilic attack, **$IrFS_3$** should exhibit a higher reaction rate than **$RhFS_3$**. On the other hand, if ligand dissociation is rate-determining, the higher effective nuclear charge at the iridium than at the rhodium atom would give rise to a slower overall reaction rate with the former metal center, as observed. Water exchange is indeed slower at Ir^{III} than at Rh^{III}: $k^{298}([Rh(H_2O)_3(\eta^5\text{-}Me_5C_5)]^{2+}) = 16 \cdot 10^4\ s^{-1}$ [30] and as $k^{298}([Ir(H_2O)_3(\eta^5\text{-}Me_5C_5)]^{2+}) = 2.53 \cdot 10^4\ s^{-1}$ [30].

3.3. *Relative Reactivities of* **$RhFS_1$**, **$RhFS_2$** *and* **$RhFS_3$**. Earlier studies showed that the tris-acetonitrile species, *e.g.* $[Rh(MeCN)_3(Htriphos)](CF_3SO_3)_3$ (**$RhHS_3$**) is a more efficient catalyst for the acetalization reaction [12] than the corresponding bis-acetonitrile species $[RhCl(MeCN)_2(Htriphos)](CF_3SO_3)_2$ (**$RhHS_2$**), and the latter, in turn, is more active than the corresponding mono-acetonitrile species $[RhCl_2(MeCN)(Htriphos)](CF_3SO_3)$ (**$RhHS_1$**). It follows that, also in the CF_3triphos-containing series of complexes, one would expect the reactivity order to be **$RhFS_3$** > **$RhFS_2$** > **$RhFS_1$**. However, accurate kinetic data for this series of complexes could not be obtained. First, as mentioned above, the tris-acetonitrile complex **$RhFS_3$** rapidly decomposes [20] under the experimental conditions used and, therefore, species other than $[RhL_3(CF_3triphos)]^{3+}$ (L = MeCN, or RR′CO or RR′O) will be present and may be involved in the catalytic cycle. Second, it was not possible to prepare solutions containing exclusively $[RhCl(MeCN)_2(CF_3triphos)](CF_3SO_3)_2$ (**$RhFS_2$**). The reaction of $[RhCl_3(CF_3triphos)]$ (**$RhFCl_3$**) with 2 equiv. $AgCF_3SO_3$ used for this purpose gave solutions invariably contaminated with a small amount of either **$RhFS_1$** or **$RhFS_3$**.

The mechanistic pathways proposed for the acetalization reactions [12] are based on the assumption that each reactant coordinates independently to the metal center before reacting with each other. The question that then arises is whether the dichloro species $[MCl_2XS_1]$ (X = CF_3triphos, Htriphos; M = Rh, Ir) exert their catalytic activity by a mechanism involving the metal activation of only one of the reagents. Alternatively, Cl^- could dissociate from $[MCl_2XS_1]$ (*Eqn. 1*) before acting as a catalyst.

$$[MCl_2L\ (tripod)]^+ + L \longrightarrow [MClL_2(tripod)]^{2+} + Cl^- \quad (1)$$

(L = MeOH, or RR′C=O, or RR′O).

As donor solvent and reagent molecules are present, a catalytically significant amount of the monohalogen species $[MClXS_2]$ may well be formed in this reaction. Related studies on the dependence of the acetalization rate of $[Ru(MeCN)_3\{PhP(CH_2CH_2PPh_2)_2\}](CF_3SO_3)_2$ in the presence of varying amounts of added Cl^- [15] indicate that, at least in this system, reactions of the type shown in *Eqn. 1* do occur under catalytic conditions.

The likelihood that, when **$RhFS_1$** is used, the actual catalyst is $[RhClL_2(CF_3triphos)]^{2+}$, coupled with the practical problems associated with **$RhFS_2$** and **$RhFS_3$** mentioned above, did not allow meaningful quantitative comparison of the overall reaction rates for these three precursors.

3.4. *Activities of the Trichloro Complexes.* The catalytic activities of the uncharged trichloro complexes $[MCl_3(tripod)]$ (M = Rh, Ir; tripod = CF_3triphos, Htriphos) can be explained by postulating that, in the presence of coordinating solvent and reagent molecules, trichloro species form first the monocationic complexes $[RhCl_2L(tripod)]^+$ which react further to the dicationic complexes $[RhClL_2(tripod)]^{2+}$ (L = ROH, or RR′C=O, or RR′O). The latter species (see above) could then be the actual catalyst.

It is noteworthy that the CF_3triphos-containing trichloro complexes **$RhFCl_3$** and **$IrFCl_3$** demonstrated lower reaction rates than **$RhHCl_3$** and **$IrHCl_3$**, respectively (see *Fig. 4*). Two factors may be responsible for these observations. First, the activation energy for chloride dissociation (*Eqn. 2*) is higher than for the M–NCMe

dissociation (*Eqn. 3*), since the M–Cl bonds being stronger than the M–NCMe bond in the complex $[RhCl(MeCN)_2(Htriphos)](CF_3SO_3)_2$ [32]. Second, the effective nuclear charge on the intermediate $[MCl_2(CF_3triphos)]^+$ will be higher than that at $[MCl_2(Htriphos)]^+$, causing the equilibrium shown in *Eqn. 4* to be shifted to the left to a larger extent for the uncharged species $[MCl_3(CF_3triphos)]$ than for $[MCl_3(Htriphos)]$.

$$[MCl_3(tripod)] \longrightarrow [MCl_2(tripod)]^+ + Cl^- \quad (2)$$

$$[M^{(z+)}L_3(tripod)]^{2+} \rightarrow [M^{(z+)}L_2(tripod)]^{z+} + L \quad (3)$$

$$[MCl_3(tripod)] + L \rightleftarrows [MCl_2L(tripod)]^+ + Cl^- \quad (4)$$

$$(L = MeOH, \text{ or } RR'C{=}O, \text{ or } RR'O).$$

The equilibrium of *Eqn. 4* is coupled with that shown in *Eqn. 1*, where similar effects also apply. As a consequence, the actual amount of catalyst, *i.e.*, $[MClL_2(tripod)]^{2+}$, at a given concentration of precursor, will be lower for CF_3triphos than for Htriphos.

4. Conclusions. – The results described above show that the catalytic activity of complexes of the type $[M^{(z+)}L_3(tripod)](CF_3SO_3)_z$ can be modulated by addition of appropriate substituents at the terminal aryl groups of the tripod ligand. It is also shown that the main advantage of the tripod ligand with the CF_3 substituents is that it allows the catalytic acetalization of benzophenone. However, further experiments will be required to optimize that reaction and extend it to other diaryl ketones.

M. S. carried out this work during his tenure as a *Research Fellow* of the *Swiss National Science Foundation*.

Experimental Part

General. The catalyst precursors $[Ru(MeCN)_3(Htriphos)](CF_3SO_3)_2$ (**RuHS$_3$**) [21], $[Ru(MeCN)_3(CF_3triphos)](CF_3SO_3)_2$ (**RuFS$_3$**) [19], $[RhCl_3(Htriphos)]$ (**RhHCl$_3$**) [23][24], $[RhCl_3(CF_3triphos)]$ (**RhFCl$_3$**) [20], $[RhCl_2(MeCN)(Htriphos)](CF_3SO_3)$ (**RhHS$_1$**) [12][22], $[RhCl_2(MeCN)(CF_3triphos)](CF_3SO_3)$ (**RhFS$_1$**) [20], $[RhCl(MeCN)_2(Htriphos)](CF_3SO_3)_2$ (**RhHS$_2$**) [12][22], $[RhCl(MeCN)_2(CF_3triphos)](CF_3SO_3)_2$ (**RhFS$_2$**) [20], $[Rh(MeCN)_3(Htriphos)](CF_3SO_3)_3$ (**RhHS$_3$**) [12][22], $[Rh(MeCN)_3(CF_3triphos)](CF_3SO_3)_3$ (**RhFS$_3$**) [20], $[IrCl_3(CF_3triphos)]$ (**IrFCl$_3$**) [19], $[IrCl_3(Htriphos)]$ (**IrHCl$_3$**) [19][23][25][26], $[Ir(MeCN)_3(Htriphos)](CF_3SO_3)_3$ (**IrHS$_3$**) [19], and $[Ir(MeCN)_3(CF_3triphos)](CF_3SO_3)_3$ (**IrFS$_3$**) [19] were prepared as described in the appropriate reference. The solvents and reagents were purchased from *Fluka AG* and used as received. Reactions were followed and yields were determined by GC, with mesitylene as an internal standard, unless otherwise noted. The GC samples were prepared by neutralizing a small aliquot taken from the reaction by filtration over neutral Al_2O_3. Analysis of samples immediately after the addition of Al_2O_3 and 24 h later showed that this treatment stopped the reaction.

Acetalization Reactions in the Presence of a Drying Agent. The catalyst precursor (2.5 μmol) was added to a CH_2Cl_2 soln. containing the aldehyde (or ketone) (5 mmol), MeOH (or ethylene glycol) (25 mmol) and trimethyl orthoformate (MOF) (or isopropyl orthoformate (IOF)) (5 mmol). After the reaction was complete (GC monitoring), the soln. was filtered over neutral Al_2O_3.

Acetalization Reactions with H_2O-Removal by Azeotropic Distillation. The catalyst precursor (2.5 μmol) was added to a benzene soln. containing the aldehyde (or ketone) (5 mmol) and ethylene glycol (25 mmol). The soln. was refluxed under Ar and the H_2O formed collected in a *Dean-Stark* trap. After the reaction was complete (GC monitoring), the soln. was filtered over neutral Al_2O_3.

Transacetalization Reaction. The catalyst precursor (2.5 μmol) was added to a CH_2Cl_2 soln. containing the aldehyde (or ketone) (5 mmol) and the acetal (5 mmol). After the reaction was complete (GC monitoring), the soln. was filtered over neutral Al_2O_3.

Acetalization of Benzophenone. The catalyst precursor (**RhFS$_1$**) (7.0 mg, 5 μmol) was added to a CH_2Cl_2 (10 ml) soln. of benzophenone (1.82 g, 10 mmol), MeOH (1.60 g, 2.0 ml, 50 mmol), and MOF (2.12 g, 20 mmol). The soln. was stirred for 5 days at r.t. (GC monitoring). Then, the soln. was filtered over neutral Al_2O_3 and evaporated. The crude product was recrystallized from CH_2Cl_2/MeOH: 1.95 g (80%) of 1,1′-(dimethoxymethylene)bis[benzene]. ^{1}H-NMR (250.13 MHz, $CDCl_3$, r.t.): 7.41 (*m*, 2 C_6H_5); 3.17 (*s*, 2 MeO).

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Received December 20, 2000