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Hydrogen-Transfer Catalytic Synergism in Binuclear Complexes Containing 2,2′-Biimidazolate as a Bridging Ligand

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The binuclear compounds $[H(CO)(PPh_3)_2Ru(\mu\text{-bim})M(COD)]$ (bim = 2,2′-biimidazolate, COD = 1,5-cyclooctadiene, M = Rh, Ir) are more active catalysts for the reduction of cyclohexanone, styrene, and α,β-unsaturated ketones (benzylideneacetophenone or benzylideneacetone), by hydrogen-transfer reactions from 2-propanol, than the mononuclear parent compounds $[RuH(Hbim)(CO)(PPh_3)_2]$ and $[M(Hbim)(COD)]$ (M = Rh, Ir). For the reduction of benzylideneacetone catalyzed by $[H(CO)(PPh_3)_2Ru(\mu\text{-bim})Ir(COD)]$, the experimental kinetic data are in accordance with an expression of the form $-d[\text{benzylideneacetone}]/dt = k[\text{Ru–Ir}][\text{benzylideneacetone}]$. On the basis of these kinetic results and other experimental evidence, a mechanism for this reaction is proposed. The full catalytic cycle involves binuclear species. The hydrogen transfer proceeds via the ruthenium atom, while the iridium center acts as the core of a metal–ligand complex of variable electron density.

Introduction

Previous studies on homogeneous catalysis by multicomponent metal systems have shown an enhancement of catalytic activity when compared to that of the individual components;[1] this enhancement effect has played an important role in the development of homogeneous polymetallic catalysts.[2] From a mechanistic point of view, it has been generally assumed that this type of catalysis involves multiple-site mechanisms.[3,4] In some cases, it has been proposed that the flexibility of M–L–M′ bridges permits the transfer of an atom or ligand from one metal center to the other.[5] However, we have recently reported that, for the reduction of cyclohexene by molecular hydrogen catalyzed by heterobimetallic Ru–Ir compounds containing azolate ligands as bridges, the reaction proceeds via only one metal and the other metal acts as the core of a metal–ligand–complex of variable electron density.[6]

Although, reduction reactions of unsaturated organic substrates with molecular hydrogen are very effective, and they have played a key role in the fundamental understanding of catalytic reactions, in some cases the use of hydrogen-transfer catalysts can produce interesting selectivity behavior.[7,8] Thus, these reactions must be viewed as a viable alternative to the classical reduction reactions with molecular hydrogen.

There are only a few examples of homogeneous polymetallic catalysts for hydrogen-transfer reactions, mainly tri- and tetranuclear iron and ruthenium clusters.[9–14] Bhaduri and Sharma[13] have found that, with 2-propanol as donor, $[H_4Ru_4(CO)_8(P^nBu_3)_4]$ catalyzes the reduction of α,β-unsaturated aldehydes to the corresponding unsaturated alcohols with high selectivities, and some kinetic studies seem to indicate involvement of cluster intermediates. Most recently, we have observed, also on the basis of kinetic experiments, that, for the hydrogen transfer from 2-propanol to cyclohexanone catalyzed by the heterobimetallic compounds $[H(CO)(PPh_3)_2Ru(\mu\text{-Cl})(\mu\text{-pz})M(TFB)]$ (M = Rh, Ir; pz = pyrazolate; TFB = tetrafluorobenzobarrelene), the nuclearity of the catalyst precursor is constant during the catalyzed reaction.[15]

As a continuation of our work on the homogeneous catalytic reduction of organic substrates by binuclear complexes,[6,15] we describe in the present paper the results of a study on the catalytic transfer activity of the heterobimetallic compounds $[H(CO)(PPh_3)_2Ru(\mu\text{-bim})M(COD)]$ (M = Rh, Ir; bim = dianion 2,2′-biimidazolate; COD = 1,5-cyclooctadiene), which are more active than the mononuclear parent compounds $[RuH(Hbim)(CO)(PPh_3)_2]$ and $[M(Hbim)(COD)]$ (M = Rh, Ir), and the kinetic study of the hydrogen transfer from 2-propanol to benzylideneacetone catalyzed by $[H(CO)(PPh_3)_2Ru(\mu\text{-bim})Ir(COD)]$. Part of this work has been subject of a preliminary communication.[16]

Results and Discussion

Table I summarizes the results for the hydrogen-transfer reactions from 2-propanol to cyclohexanone, sytrene, benzylideneacetophenone, and mixtures of cyclohexanone/styrene (1:1) catalyzed by the heterobimetallic compounds $[H(CO)(PPh_3)_2Ru(\mu\text{-bim})M(COD)]$ (M = Rh,

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Table I. Hydrogen-Transfer Reactions from 2-Propanol[a]

catalyst	substrate (A)	time, h	mol of AH_2/mol of M[b,c]	AH_2
"Ru(μ-bim)Ir"[b]	cyclohexanone	8	80	cyclohexanol
	styrene	9	1.0	ethylbenzene
	benzylideneacetophenone	8	57.0	1,3-diphenylpropan-1-one
	cyclohexanone/styrene (1:1)	23	13.5	cyclohexanol
			2.0	ethylbenzene
"Ru(μ-bim)Rh"[c]	cyclohexanone	8	76.0	cyclohexanol
	styrene	9	2.5	ethylbenzene
	benzylideneacetophenone	8	92.5	1,3-diphenylpropan-1-one
	cyclohexanone/styrene (1:1)	23	13.5	cyclohexanol
			2.0	ethylbenzene
[RuH(Hbim)(CO)(PPh_3)$_2$]	cyclohexanone	24	5.5	cyclohexanol
	styrene	9		ethylbenzene
	benzylideneacetophenone	8	4.5	1,3-diphenylpropan-1-one
[Rh(Hbim)(COD)]	cyclohexanone	24	0.5	cyclohexanol
	styrene	9	0.5	ethylbenzene
	benzylideneacetophenone	8	2.0	1,3-diphenylpropan-1-one
[Ir(Hbim)(COD)]	cyclohexanone	24	0.5	cyclohexanol
	styrene	9		ethylbenzene
	benzylideneacetophenone	8	2.0	1,3-diphenylpropan-1-one

[a] Reaction conditions: [M] = 2.5×10^{-3} M; [A]/[M] = 100. Preactivation time: 1 h. Solvent: 2-propanol; temperature 83 °C. [b] M = Ru + Ir. [c] M = Ru + Rh.

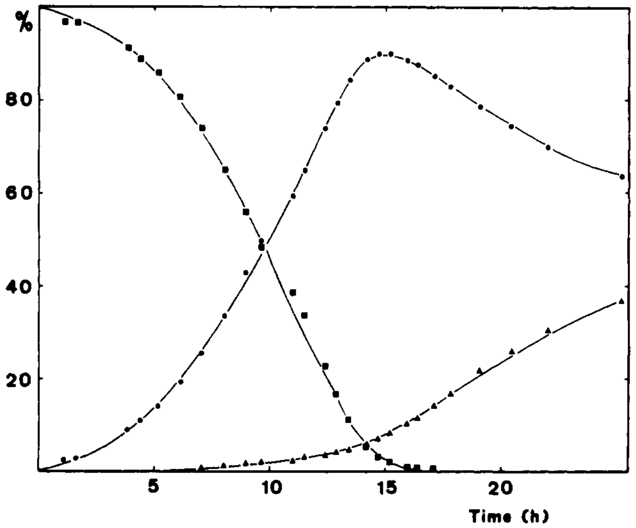

Figure 1. Hydrogen transfer from 2-propanol to benzylideneacetone catalyzed by [H(CO)(PPh_3)$_2$Ru(μ-bim)Ir(COD)]. Reaction conditions: [catalyst] = 2.3×10^{-3} M, [benzylideneacetone] = 0.13 M. Temperature: 83 °C. Preactivation time: 1 h. Solvent: 2-propanol/toluene (7:1). Key: (■) benzylideneacetone; (●) 4-phenylbutan-2-one; (▲) 4-phenylbutan-2-ol.

Ir). Reactions were performed in 2-propanol as solvent at 83 °C and 1 atm of nitrogen pressure. For comparison, the activities of the mononuclear complexes [RuH(Hbim)(CO)(PPh_3)$_2$] and [M(Hbim)(COD)] (M = Rh, Ir) are also included.

The heterobimetallic compounds are clearly more active catalysts for this type of reactions than the mononuclear complexes. Cyclohexanone is more rapidly reduced than styrene, and this is also true in a competitive sense. However, the results reported in Table I and Figure 1 show that the reduction of the C=C bond of α,β-unsaturated ketones is preferred to the reduction of the C=O bond. Although for the reduction of unsaturated ketones two reaction paths can be envisaged (C=C reduction or C=O reduction), it was observed by careful GC measurements that, in this case, no unsaturated alcohol is formed. A similar phenomenon was previously observed in our laboratory for the same reactions catalyzed by the tetrahydrides [MH_4(CO)(P^iPr_3)$_2$] (M = Ru, Os).[7] Then, we suggested that the C=C and C=O bond conjugation in α,β-unsaturated ketones may decrease both the coordination ability of the carbonyl group and the susceptibility of hydride attack on the carbon atom of the carbonyl group compared to saturated carbonyl compounds.[17] In this line the complex [OsHCl(CO)(η^2-CH_2=CH_2COCH_3)(P^iPr_3)$_2$] was isolated.[18]

Table II. Kinetic Data for the Reduction of Benzylideneacetone to 4-Phenylbutan-2-one by Hydrogen Transfer from 2-Propanol, Catalyzed by [H(CO)(PPh_3)$_2$Ru(μ-bim)Ir(COD)][a]

[Ru–Ir], 10^3 M	[benzylideneacetone], M	r_0, 10^6 M s^{-1}	k_{obs}, 10^3 s^{-1}	k_5, 10^3 M^{-1} s^{-1}
1.0	0.25	1.6	1.60	6.4
1.2	0.25	2.0	1.67	6.7
1.5	0.25	2.3	1.53	6.1
1.9	0.25	3.2	1.68	6.7
1.2	0.17	1.1	0.92	5.4
1.2	0.19	1.6	1.33	7.0
1.2	0.24	1.9	1.58	6.6
1.2	0.32	2.3	1.92	6.0

[a] In 2-propanol/toluene (7:1) at 83 °C. Preactivation time: 1 h.

The heterobimetallic complexes were recovered unchanged after the catalytic reactions, suggesting that the catalytic cycles of these processes could involve binuclear intermediates. In order to support this hypothesis, a kinetic and spectroscopic investigation of the reduction reaction of benzylideneacetone catalyzed by [H(CO)(PPh_3)$_2$Ru(μ-bim)Ir(COD)] was carried out.

Kinetic Study of the Reduction of Benzylideneacetone Catalyzed by [H(CO)(PPh_3)$_2$Ru(μ-bim)Ir(COD)]. Figure 1 summarizes the course of a typical reaction. It shows a slight induction period which does not substantially change when the catalyst is treated with 2-propanol, for 1 h at 83 °C, before benzylideneacetone is added. Initial rates collected in Table II were determined after the corresponding induction period.

A simple rate law for the catalytic hydrogen-transfer reaction

$$DH_2 + A \xrightarrow{Cat} D + AH_2 \qquad (1)$$

is

$$-d[A]/dt = k_2[DH_2]^m[Cat]^n[A]^q \qquad (2)$$

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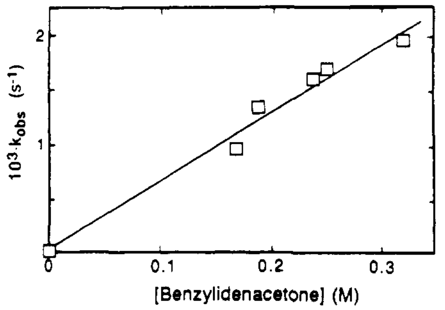


Figure 2. Rate constant for the hydrogen transfer from 2-propanol to benzylideneacetone catalyzed by [H(CO)-$(PPh_3)_2Ru(\mu\text{-bim})Ir(COD)$] in 2-propanol/toluene (7:1) at 83 °C.

When the donor DH_2 acts as reaction solvent, this rate law can be simplified to

$$-d[A]/dt = k_3[Cat]^n[A]^q \qquad (3)$$

In order to determine the rate dependence on the various reaction components, hydrogen-transfer runs were performed at different catalyst and substrate ([A]) concentrations. Plots of log (−d[A]/dt) versus log [Cat] yield straight line of slope 1.0, showing that the reduction of benzylideneacetone is first order in catalyst concentration. The values of k_{obs} collected in Table II were thus obtained from eq 4 for $n = 1$. Plots of log (−d[A]/dt) versus log

$$-d[A]/dt = k_{obs}[Cat]^n \qquad (4)$$

[benzylideneacetone] yield a straight line of slope 1.1, demonstrating that the reaction is also first order in substrate concentration (i.e., $q = 1$ in eq 3). The catalytic rate law therefore is

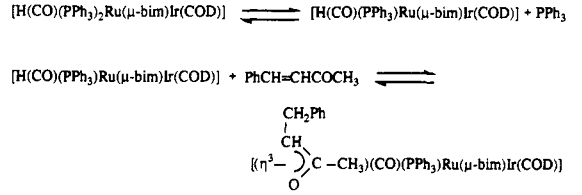
$$-d[\text{benzylideneacetone}]/dt = k_5[Cat][\text{benzylideneacetone}] \qquad (5)$$

and $k_{obs} = k_5$[benzylideneacetone].

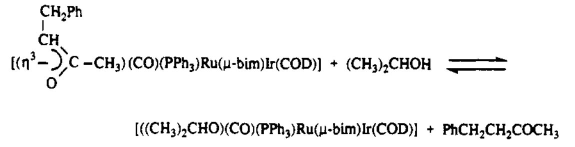
A plot of k_{obs} versus [benzylideneacetone] (Figure 2) yields a value for k_5, at 83 °C, of $(6.3 \pm 0.5) \times 10^{-3}$ M^{-1} s^{-1}.

Comments on the Hydrogen-Transfer Mechanism. In order to obtain more information about the possible mechanism of the catalysis, a spectroscopic study of the catalytic reaction was carried out. The ^{31}P NMR spectra of the catalytic solutions, before benzylideneacetone is added, show an only signal at 49.27 ppm, assigned to the complex [$H(CO)(PPh_3)_2Ru(\mu\text{-bim})Ir(COD)$] by comparison of these spectra with that of a pure sample.[19] The ^{31}P NMR of the catalytic solutions of different runs, after the benzylideneacetone was added, showed also the same signal. This, together with the first-order dependence of the rate on the concentration of catalyst, eliminates the possibility of [$H(CO)(PPh_3)_2Ru(\mu\text{-bim})Ir(COD)$] breaking down to mononuclear catalytically active species. On the other hand, as it has been above mentioned, the heterobimetallic compound was recovered unchanged after the catalytic reactions, indicating that the 1,5-cyclooctadiene ligand coordinated to the iridium atom is not reduced. It is known, from other studies, that the hydrogen-transfer reactions catalyzed by iridium olefin complexes proceed via hydride intermediates, involving the isomerization or reduction of the coordinated olefin.[20] So, it seems possible to assert that the ruthenium atom could be the only active center, similarly to that observed for the cyclohexene reduction, by molecular hydrogen, catalyzed by the same complex.[6] Assuming that the ruthenium atom is the active center and it is coordinatively saturated, the creation of a coordination vacancy must be necessary for catalysis. Thus, we think that, although species [$H(CO)(PPh_3)Ru(\mu\text{-bim})Ir(COD)$] could not be detected by spectroscopic methods, they should be formed in no detectable concentration during the induction period. In accordance with this, we have observed that (i) the rate of formation of saturated ketone was found to be inhibited by the addition of PPh_3 and (ii) the addition of an equimolecular amount of [$H(CO)\{P(p\text{-Tol})_3\}_2Ru(\mu\text{-bim})Ir(COD)$] to a 2-propanol/toluene solution of [$H(CO)(PPh_3)_2Ru(\mu\text{-bim})Ir(COD)$] leads to the formation of the mixed [$H(CO)\{P(p\text{-Tol})_3\}(PPh_3)Ru(\mu\text{-bim})Ir(COD)$]. Thus, the following set of reactions are proposed for the catalytic cycle:

$$[H(CO)(PPh_3)_2Ru(\mu\text{-bim})Ir(COD)] \rightleftharpoons [H(CO)(PPh_3)Ru(\mu\text{-bim})Ir(COD)] + PPh_3 \qquad (6)$$



$$[H(CO)(PPh_3)Ru(\mu\text{-bim})Ir(COD)] + PhCH{=}CHCOCH_3 \rightleftharpoons [(\eta^3\text{-}\overset{\overset{CH_2Ph}{|}}{CH}{\cdots}C(\cdots O)\text{-}CH_3)(CO)(PPh_3)Ru(\mu\text{-bim})Ir(COD)] \qquad (7)$$



$$[(\eta^3\text{-}\overset{\overset{CH_2Ph}{|}}{CH}{\cdots}C(\cdots O)\text{-}CH_3)(CO)(PPh_3)Ru(\mu\text{-bim})Ir(COD)] + (CH_3)_2CHOH \rightleftharpoons [((CH_3)_2CHO)(CO)(PPh_3)Ru(\mu\text{-bim})Ir(COD)] + PhCH_2CH_2COCH_3 \qquad (8)$$

$$[((CH_3)_2CHO)(CO)(PPh_3)Ru(\mu\text{-bim})Ir(COD)] \rightleftharpoons [H(CO)(PPh_3)Ru(\mu\text{-bim})Ir(COD)] + (CH_3)_2CO \qquad (9)$$

This mechanism is consistent with the kinetic results above described. Because the catalysis proceeds via only one metal, the mechanism is analogous to that previously reported by us for the same reaction catalyzed by [$RuHCl(CO)(P^iPr_3)_2$].[17] The formation of a π-oxaallyl intermediate had been previously proposed in certain reactions of iron,[21] ruthenium,[22-24] and cobalt,[25] and most recently the photochemical formation of some (π-oxaallyl)molybdenum and -tungsten complexes has been reported.[26]

Concluding Remarks. This study has shown that the heterobimetallic compounds [$H(CO)(PPh_3)_2Ru(\mu\text{-bim})Ir(COD)$] are more active catalysts than the mononuclear parent compounds, not only for cyclohexene hydrogenation but also for the hydrogen transfer from 2-propanol to ketones and α,β-unsaturated ketones. Similarly to cyclohexene hydrogenation, the hydrogen transfer proceeds via one metal, and the other metal acts as the core of a metal–ligand complex of variable electron density. In conclusion, the above mentioned results have revealed experimental evidence of hydrogen-transfer catalytic synergism by indirect cooperative effects between metallic centers of binuclear complexes containing 2,2′-biimidazolate as a bridging ligand.

Experimental Section

General Comments. All manipulations were conducted with rigorous exclusion of air. Solvents were dried by known procedures

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and distilled under nitrogen prior to use. Cyclohexanone, benzylideneacetophenone, and benzylideneacetone (Merck) were used without further purification. Styrene (Merck) was passed through an alumina column.

Physical Measurements. ^{1}H NMR spectra were recorded on a Varian UNYT 300 spectrophotometer at 299.949 MHz, and ^{31}P{^{1}H}NMR spectra were recorded on a Varian XL 200 spectrophotometer at 80.984 MHz; chemical shifts are expressed in parts per million upfield from $Si(CH_3)_4$ (^{1}H) and phosphoric acid at 85% as external references. Samples for recording the ^{31}P{^{1}H} NMR spectra were prepared in 5-mm-diameter tubes under the same conditions employed for the catalytic reactions. These samples were then introduced into 1-cm-diameter tubes containing $CDCl_3$. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer.

The analysis of the products of the catalytic reactions was carried out on a Perkin-Elmer 3920 B chromatograph, connected to a Perkin-Elmer M-2 calculation integrator, using an FFAP on Chromosorb GHP 80/100 mesh (3.6 m × 1.8 in) column, at 120 °C (cyclohexanone and styrene) and 240 °C (benzylideneacetophenone). For the reactions with benzylideneacetone we used a Perkin-Elmer 8500 gas chromatograph with a flame ionization detector and the same FFAP column, at 260 °C. The reduction products were identified by comparison of their retention times with those observed for pure samples. Initial rate data were fitted by conventional linear regression methods.

Materials. Complexes $[H(CO)(PPh_3)_2Ru(\mu\text{-bim})M(COD)]$ (M = Rh, Ir),[19] $[RuH(Hbim)(CO)(PPh_3)_2]$,[19] and $[M(Hbim)(COD)]$ (M = Rh, Ir)[27] were prepared by published methods. Complexes $[RuH(Hbim)(CO)\{P(p\text{-Tol})_3\}_2]$ and $[H(CO)\{P(p\text{-Tol})_3\}_2Ru(\mu\text{-bim})Ir(CO)]$ were prepared by the same procedures described for the analogous complexes with PPh_3.[19] IR and NMR spectroscopic data for $[RuH(Hbim)(CO)\{P(p\text{-Tol})_3\}_2]$: IR (Nujol mull) ν_{N-H} 2800–2300 cm^{-1} (br), ν_{Ru-H} 1950 cm^{-1} (m), ν_{CO} 1925 cm^{-1} (s); ^{1}H NMR (C_6D_6, 20 °C) δ −10.84 (t, J = 20.4 Hz, 1 H, Ru–H), 1.91 (s, 18 H, 6 Me, *p*-tolyl groups), 6.33 (s, 1 H), 6.52 (s, 1 H), 6.76 (s, 1 H) (3, =CH, bim), 6.87 (d, 12 H, C_6H_4), 7.19 (s, 1 H, =CH, bim), 7.65 (m, 12 H, C_6H_4); ^{31}P{^{1}H}NMR (C_6D_6, 20 °C) δ 46.65 (s). IR and NMR spectroscopic data for $[H(CO)\{P(p\text{-Tol})_3\}_2Ru(\mu\text{-bim})Ir(COD)]$: IR (Nujol mull) ν_{Ru-H} 1990 cm^{-1} (m), ν_{CO} 1915 cm^{-1} (s); ^{1}H NMR (C_6D_6, 20 °C) δ −12.75 (t, J = 19.4 Hz, 1 H, Ru–H), 1.42 (m, 4 H, CH_2, COD), 2.05 (s, 18 H, 6 Me, *p*-tolyl groups), 2.20 (m, 4 H, CH_2, COD), 3.94 (m, 4 H, =CH, COD), 6.02 (s, 1 H), 6.15 (s, 1 H), 6.37 (s, 1 H) (3, =CH, bim), 6.92 (d, 12 H, C_6H_4), 6.96 (s, 1 H, =CH, bim), 7.65 (m, 12 H, C_6H_4); ^{31}P{^{1}H} NMR (toluene/$CDCl_3$, 20 °C) δ 46.99 (s).

Reaction of $[H(CO)(PPh_3)_2Ru(\mu\text{-bim})Ir(COD)]$ with $[H(CO)\{P(p\text{-Tol})_3\}_2Ru(\mu\text{-bim})Ir(COD)]$. To a NMR tube containing a toluene/2-propanol (1:3) solution of $[H(CO)(PPh_3)_2Ru(\mu\text{-bim})Ir(COD)]$ (16.5 mg, 0.015 mmol) was added an equimolar amount of $[H(CO)\{P(p\text{-Tol})_3\}_2Ru(\mu\text{-bim})Ir(COD)]$ (17.7 mg, 0.015 mmol). The sample was shaken and then immersed in a bath at 60 °C. The reaction was followed by ^{31}P{^{1}H} NMR spectroscopy. Before heating the mixture, the spectrum showed only the two singlets of the starting materials at 49.27 and 46.99 ppm respectively. After 12 h, there was also an AB system characterized by two signals at 48.40 and 47.96 ppm, which is assigned to the mixed $[H(CO)\{P(p\text{-Tol})_3\}(PPh_3)Ru(\mu\text{-bim})Ir(COD)]$.

Hydrogen-Transfer Reactions from 2-Propanol to Cyclohexanone, Styrene, or Benzylideneacetophenone. The reactions were carried out under nitrogen in refluxing 2-propanol with magnetic stirring. The equipment consisted of a 50-mL two-necked flask fitted with a Suba-seal to allow samples to be removed without opening the system. In a typical procedure, a solution of the catalyst (0.02 mmol, if it is mononuclear, or 0.01 mmol, if it is heterobinuclear) in 4 mL of 2-propanol was refluxed for 1 h and a solution of the corresponding substrate (2 mmol) in 4 mL of 2-propanol was then injected.

Kinetics of the Hydrogen-Transfer Reaction from 2-Propanol to Benzylideneacetone. The reactions were carried out, in the equipment above described, under nitrogen atmosphere, in a refluxing mixture of 2-propanol and toluene (7:1). In a typical procedure, a solution of $[H(CO)(PPh_3)_2Ru(\mu\text{-bim})Ir(COD)]$ in 1 mL of toluene and 3 mL of 2-propanol was refluxed for 1 h, and a solution of benzylideneacetone in 4 mL of 2-propanol was then injected. Initial rates collected in Table II were calculated after the induction periods.

For the reactions in the presence of triphenylphosphine the procedure was as follows: To a solution of the catalyst (0.01 mmol) in 1 mL of toluene was added a PPh_3 solution 1.4×10^{-3} M in 2-propanol and 2 mmol of the substrate in the appropriate amount of 2-propanol to complete a total volume of 8 mL. The initial rates observed were 0.6×10^{-6}, 0.5×10^{-6}, and 0.3×10^{-6} M·s^{-1}, for triphenylphosphine concentrations of 0.4×10^{-4}, 0.9×10^{-4}, and 1.7×10^{-4} M, respectively.

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