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Dehydrogenation of Alcohols by Bis(phosphinite) Benzene Based and Bis(phosphine) Ruthenocene Based Iridium Pincer Complexes

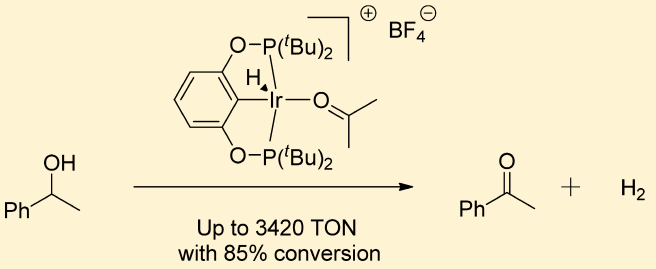
Alexey V. Polukeev,[†] Pavel V. Petrovskii,[†,§] Alexander S. Peregudov,[†] Mariam G. Ezernitskaya,[†] and Avthandil A. Koridze*[,†,‡]

[†]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street, 119991 Moscow, Russian Federation

[‡]Institute of Organometallic Chemistry, I. Javakhishvili Tbilisi State University, 3 Chavchavadze Avenue, 0128 Tbilisi, Georgia

Supporting Information

ABSTRACT: Dehydrogenation of alcohols by three iridium pincer complexes, IrH(Cl)[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$] (**1**), {IrH(acetone)[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$]}{BF$_4$} (**2**), and IrH(Cl)[{2,5-(^{t}Bu$_2$PCH$_2$)$_2$C$_5$H$_2$}Ru(C$_5$H$_5$)] (**3**), is reported, in both the presence and the absence of a sacrificial hydrogen acceptor. Dehydrogenation of secondary alcohols proceeds in a catalytic mode with turnover numbers up to 3420 (85% conversion) for acceptorless dehydrogenation of 1-phenylethanol. Primary alcohols are readily decarbonylated even at room temperature to give catalytically inactive 16e Ir−CO adducts. The mechanism of this transformation was studied in detail, especially for EtOH; new intermediates were isolated and characterized.



INTRODUCTION

Hydrogen is potentially an ideal energy carrier, as it is nonpolluting and has a high energy density by weight. In view of global concerns regarding the environment and sustainable energy resources, hydrogen is often considered as the fuel of the future, a promising candidate to solve the problems caused by the use of fossil fuels.[1] The production, storage, and transportation of hydrogen have attracted careful attention in recent decades.[2] To preserve the important advantages of liquid fuels such as gasoline and diesel, namely relative safety, fast refilling times, and high energy density, it would be of great interest to achieve hydrogen storage in liquid materials. Significant efforts are devoted to the development of catalysts able to dehydrogenate some hydrogen-rich liquids ("organic hydrides") such as alkanes,[3] formic acid,[4] and nitrogen heterocycles.[5] In this respect, alcohols seem to hold considerable promise.[6]

On the other hand, dehydrogenation may be considered as a kind of oxidation of alcohols to aldehydes and ketones, which is an important transformation in synthetic organic chemistry.[7] Transition-metal-catalyzed dehydrogenative oxidation of alcohols is tantalizing in view of the development of environmentally friendly, high-atom-economy processes.[8−10] Carbonyl compounds generated usually have a much wider range of reactivity and are of higher value. They can be functionalized in situ to form a substrate for hydrogenation, to which catalyst returns taken hydrogen (so-called borrowing hydrogen strategy),[8,9] or alternatively hydrogen can be liberated or transferred to a sacrificial hydrogen acceptor.[10] A number of transition-metal complexes able to provide transfer dehydrogenation of alcohols are known, with O$_2$,[11] H$_2$O$_2$,[12] carbonyl compounds,[13] and alkenes[14] being used as hydrogen acceptors. The most desired acceptorless alcohol dehydrogenation is a less common case.[10] Several systems capable of acceptorless dehydrogenation of alcohols have been developed using rhodium,[15] ruthenium,[16] and iridium[17] catalysts. While some of them appeared promising toward "green" synthesis,[18] their activity should be further improved to produce a commercial process for hydrogen generation and storage based on transformations of organic molecules.[6]

Furthermore, in the case of primary alcohols, the dehydrogenation reaction is often complicated by decarbonylation of the corresponding aldehyde,[14b,19] which leads to catalyst deactivation. Decarbonylation of secondary alcohols is rarely observed.[20] These processes are generally believed to proceed via formation of acyl complexes followed by migratory deinsertion of CO;[19c,d,g,20] however, few intermediates were isolated and characterized.[19c,g]

Earlier, a family of benzene-, anthracene-, and metallocene-based iridium pincer complexes have been shown to be the most productive catalysts for the dehydrogenation of alkanes.[3,21] One of these catalysts, namely IrH$_2$[2,6-(^{t}Bu$_2$PCH$_2$)$_2$C$_6$H$_3$], was successfully applied to the dehydrogenation of alcohols. Thus, it catalyzed the transfer dehydrogenation of primary and secondary alcohols with *tert*-butylethylene (tbe) as a hydrogen acceptor to form the corresponding aldehydes and ketones and *tert*-butylethane in excellent yields (however, with low turnover numbers, TONs),[14b] indicating that iridium pincer complexes have

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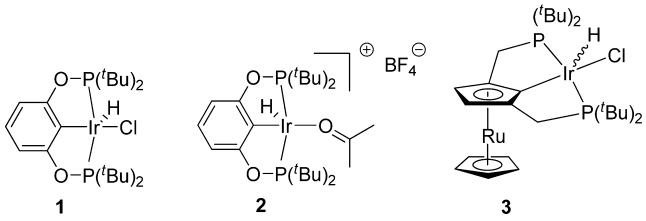
potential in this area. Indeed, a recently developed dibenzobarrelene-based complex (not tested for alkane dehydrogenation) has shown excellent activity in acceptorless dehydrogenation of alcohols.[17e] Bearing these results in mind, we decided to test counterparts of $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$, which showed higher activity in alkane dehydrogenation, in alcohol dehydrogenation.

In this paper we report catalytic dehydrogenation of alcohols by bis(phosphinite) benzene based and bis(phosphine) ruthenocene based pincer complexes. Some of these complexes have shown high activity in the acceptorless dehydrogenation of secondary alcohols; remarkably, the reaction proceeds slowly even at room temperature. Primary alcohols readily undergo decarbonylation. The mechanism of the reaction with alcohols was studied in detail, which allowed identification of some new intermediates. We hope that the results obtained will shed additional light on the processes of dehydrogenation and decarbonylation of alcohols by transition-metal complexes.

RESULTS

Synthesis of Catalysts. The known complexes **1**[3f] and **3** (the latter as a mixture of H-endo and H-exo isomers[3h]) (Chart 1) were synthesized according to the literature procedures.

Chart 1. Catalysts Tested in This Work



Cationic complex **2** was obtained by chloride abstraction from **1** using $AgBF_4$ in acetone. Its counterpart with the $B(C_6F_5)_4^-$ anion was described in the literature as a catalyst for the reduction of alkyl halides by triethylsilane;[22] complexes with other anions were generated in situ and used for hydrogen isotope exchange reactions[23] without characterization. Complex **2** reveals broadened signals in the ^1H, ^{31}P, and ^{19}F NMR spectra due to fluxional coordination of BF_4^- and acetone to the metal center in solution.[24] The IR spectrum of **2** in KBr pellets contains two $\nu(CO)$ bands at 1653 and 1637 cm^{-1} of coordinated acetone, which can be explained by solid-state interactions rather than by the existence of isomers. A solution of **2** in $CHCl_3$ reveals only the band at 1710 cm^{-1} corresponding to free acetone, indicating that, despite a broadened signal in the ^1H NMR spectrum, in solution acetone is for the most part not bound to the iridium.

Transfer Dehydrogenation of Isopropyl Alcohol. The thermodynamics of acceptorless alcohol dehydrogenation demand elevated temperatures and removal of H_2 from the equilibrium.[25,26] We first tested catalysts **1** and **3** for more favorable transfer dehydrogenation using tbe as a hydrogen acceptor. The latter was found to isomerize into the inefficient hydrogen acceptors 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene if acidic species are present in the reaction mixture;[27] this is why complex **2**, which we wanted to test without basic additives, was not used. According to the literature data,[3f] in the case of hydrido chloride complexes **1** and **3**, 1 equiv of a base is required to remove HCl from the iridium atom to give catalytically active species.

The results are summarized in Table 1. At temperatures above 200 °C for **1** (entry 1) and about 200 °C for **3** (entry 4)

Table 1. Transfer Dehydrogenation of Isopropyl Alcohol by Catalysts 1 and 3[a]

entry	cat.	substrate	T, °C	time, h	conversion, %	TON
1	**1**	^{i}PrOH	240	1	76	3040
2	**1**	^{i}PrOH	200	1	100	4000
3	**1**	^{i}PrOH	150	8	100	4000
4	**3**	^{i}PrOH	200	8	13	500
5	**3**	^{i}PrOH	150	8	38	1520
6	**3**	^{i}PrOH	150	16	44	1770
7	**3**	^{i}PrOH	110	8	9	370
8	**3**	^{i}PrOH	110	40	26	1030

[a]Conditions: 0.025 mol % of catalyst, 1.5 equiv of ^{t}BuONa, 1/1 substrate/acceptor ratio.

decarbonylation of isopropyl alcohol or acetone occurs to give the catalytically inactive carbonyl compounds $Ir(CO)[2,6\text{-}(^tBu_2PO)_2C_6H_3]$ (**4**)[3g] and $Ir(CO)[\{2,5\text{-}(^tBu_2PCH_2)_2C_5H_2\}\text{-}Ru(C_5H_5)]$ (**5**),[3h] respectively, which limits the TON. Decarbonylation as a pathway for deactivation of iridium dehydrogenation catalysts is not unexpected;[14b,17e] indeed, control experiments revealed that complex **4** possesses negligible activity. Lowering the temperature allowed us to avoid decarbonylation; thus, at 200 °C complex **1** rapidly affords 4000 TON with formation of acetone in the quantitative yield (entry 2), while at 150 °C, it takes approximately 8 h for the reaction to be completed. It should be noted that the TON obtained is 2 orders of magnitude higher than that for the related complex $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$.[14b] Complex **3** was found to be sufficiently less active than **1** under any conditions employed; lowering the temperature again allowed us to avoid decarbonylation; however, it did not much improve the results.

Acceptorless Dehydrogenation of Alcohols. Surprisingly, in the presence of 1 equiv of the base, complexes **1** and **3** are able to provide catalytic acceptorless alcohol dehydrogenation even at room temperature, although the reaction rate does not exceed 2–3 TON per day. To our knowledge, no catalyst operates under such mild conditions. As was mentioned earlier, heating is expected to improve the performance. Taking into consideration the results of transfer dehydrogenation, we limited temperatures used to 190 °C for **1** and to 150 °C for **3** to prevent decarbonylation.

Complex **1** has been shown to be an effective catalyst for acceptorless dehydrogenation of secondary alcohols (Table 2), providing approximately 2000 equiv of hydrogen/mol of catalyst for alcohols with high boiling points (entries 1 and 6). A small excess of base always present in catalytic experiments with **1** and **3** causes the formation of some amounts of Guerbet-type products in addition to the target ketones. The Guerbet reaction can be considered as dehydrogenation of an alcohol to a carbonyl compound followed by condensation of the latter and rehydrogenation.[10] Thus, under these conditions some quantity of alcohol is involved into transfer dehydrogenation and the amount of hydrogen evolved actually is smaller than the TON. The addition of more than 1.5 equiv of a base has never caused any serious changes, except for the increased formation of condensation products. In order to identify catalytically active

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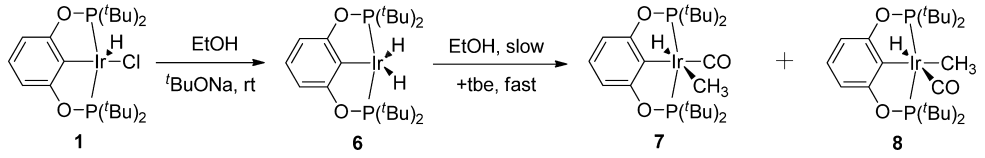
Table 2. Acceptorless Dehydrogenation of Alcohols by Catalysts 1−3 and 6[a]

entry	cat.	substrate	T, °C[b]	time, h	conversion, %	TON	amt of H_2 evolved, equiv[c]
1	**1**	$PhCH(OH)CH_3$	190	18	74[d]	2960[d]	2070
2	**6**	$PhCH(OH)CH_3$	190	18	50	2000	2000
3	**6**	$PhCH(OH)CH_3$	190	36	55	2200	2200
4	**6**	$PhCH(OH)CH_3$	175	18	28	1120	1120
5	**6**	$PhCH(OH)CH_3$	150	18	9	350	350
6	**1**	CyOH	190	18	89[e]	3560[e]	1780
7	**1**	^{i}PrOH	90	8	2	90	90
8	**1**	$PhCH(OH)CH_3$	23	24	0.1	2	2
9	**1**	^{i}PrOH	23	24	0.1	3	3
10	**1**	EtOH	90	8	0	0	
11	**1**	MeOH	90	8	0	0	
12	**3**	$PhCH(OH)CH_3$	150	18	48[d]	1920[d]	1130
13	**3**	EtOH	90	8	0	0	
14	**2**	^{i}PrOH[f]	23	24	0	0	
15	**2**	$PhCH(OH)CH_3$	190	18	71[g]	2530	2530
16	**2**	$PhCH(OH)CH_3$	190	36	85[g]	3420	3420
17	**2**	$PhCH(OH)CH_3$	175	18	43[g]	1720	1720

[a]Conditions: 0.025 mol % of catalyst, 1.5 equiv of ^{t}BuONa (except for **2** and **6**). [b]Oil bath temperature. [c]Calculated from stoichiometry on the basis of analysis of products. When this number differs from the TON, products other than the appropriate carbonyl compound are formed, leading to some contribution of transfer dehydrogenation. [d]1,3-Diphenyl-1-butanone and 1,3-diphenyl-1-butanol are formed as byproducts. [e]2-Cyclohexenyl-1-cyclohexanol and 3-cyclohexenyl-1-cyclohexanol are formed as major products. [f]In C_6D_6. [g]Trace amounts of bis(1-phenylethyl) ether and ethylbenzene are formed.

Scheme 1. Reaction of Complex 1 with EtOH



species, we synthesized dihydride $IrH_2[2,6\text{-}(^{t}Bu_2PO)_2C_6H_3]$ (**6**)[3g] and tested it in the dehydrogenation of $PhCH(OH)CH_3$ (entries 2−5). This complex was found to operate under neutral conditions and gave the same results as **1** did. Thus, complex **6** is the compound actually involved into the catalytic cycle, as it was the case for alkane dehydrogenation.[3g] However, from an experimental point of view, it is more convenient to use the air-stable hydrido chloride **1** as a catalyst precursor. Since catalysis by **6** proceeds without side reactions, we used it to optimize the reaction conditions. Thus, it was found that high temperature is required to obtain a reasonable reaction rate, which becomes negligible after 18 h of heating at 190 °C and 2000 TON obtained.

Cationic complex **2** was used without addition of base. It is inactive at ambient temperature (entry 14), but at high temperatures its activity is higher than that of **1** or **6** (entries 15−17) and diminishes slowly. Thus, after 36 h of heating it showed 3420 TON with 85% conversion in comparison to 2200 and 55% for **6**. We speculate that, at elevated temperatures, **2** is probably able to lose reversibly HBF_4 and operates via the same mechanism as **6** does. In this respect, it is worth noting that trace amounts of bis(1-phenylethyl) ether and ethylbenzene are detected in the reaction mixture when **2** is used, presumably as a result of an acid-catalyzed reaction. The improved activity of **2** may be ascribed to the destruction of some inhibiting side products: for example, products of metalation of ketones by the acid evolved. Thus, the reaction of an analogue of **6**, $IrH_2[2,6\text{-}(^{t}Bu_2PCH_2)_2C_6H_3]$, with acetophenone in the presence of norbornene was reported[28] to give the iridium acetylphenyl hydride $IrH(C_6H_4C(O)CH_3)[2,6\text{-}(^{t}Bu_2PCH_2)_2C_6H_3]$, which is sufficiently stable (apart from isomerization), at least at 135 °C.

Complex **3** again gave significantly poorer results than **1** did. Primary alcohols appeared to be unsuitable substrates because they are readily decarbonylated at room temperature by both **1** and **3**.

Decarbonylation of Primary Alcohols. Decarbonylation of EtOH. In the presence of EtOH and ^{t}BuONa, complex **1** is rapidly converted to dihydride complex **6**. Stoichiometric considerations require the formation of 1 equiv of acetic aldehyde, which, however, was not detected by NMR, presumably due to condensation. Further, dihydride **6** slowly reacts with ethanol at room temperature to form the new carbonyl hydrido methyl complex **7** and its isomer **8** (Scheme 1). No base is required at this stage; independently prepared **6** can be used instead.

Several days are required for the reaction to be completed and to provide a mixture of **7**, **8**, and carbonyl complex **4**. The addition of tbe as a hydrogen acceptor accelerates the reaction with alcohol; a mixture of **7** and **8** in a 98/2 ratio is observed after 0.5−1 h, with no starting material or decomposition products present. Compounds **7** and **8** (the latter in mixtures with **7** or **4** due to further transformations; see below) were characterized by means of NMR and IR spectra and elemental analysis. Thus, the $^{31}P\{^{1}H\}$ NMR spectrum of **7** reveals a singlet at 169.4 ppm and the characteristic hydride signal appears as triplets of quadruplets at −10.93 ppm ($^{2}J_{P-H}$ = 18.6 Hz, $^{3}J_{H-H}$ = 1.5 Hz), while in the $^{13}C\{^{1}H\}$ NMR spectrum, the

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upfield resonance corresponding to the iridium-bound methyl group is observed at −26.7 ppm. Isomeric complex **8** gives similar signals at 163.7, −9.71 ($^2J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 1.5 Hz), and −47.8 ppm (t, $^2J_{CP}$ = 3.8 Hz) in the $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectra, respectively. Unfortunately, we could not determine the structures of **7** and **8** using X-ray crystallography because of molecular disorder in the crystals obtained. For this reason, the conclusions on the relative configuration of the substituents at the iridium atom were made using NMR spectra. Thus, in the case of **7**, ^1H NOESY spectrum displayed a cross peak between the Ir-*H* and one pair of diastereotopic *tert*-butyl groups, while the methyl group bound to iridium showed a cross peak with another pair, which is consistent with a structure where the hydride and the methyl group are arranged at the opposite sides of the plane formed by the benzene ring and two five-membered chelating metallacycles. Additional proof was provided by the ^{13}C NMR spectrum without decoupling, where the CO signal exhibited a small $^1H,^{13}C$ spin−spin coupling of ca. 4 Hz, which is strongly indicative of a mutually cis arrangement of CO and hydride ligands.[24] For complex **8**, there is also a cross peak between the Ir-*H* and one pair of diastereotopic *tert*-butyl groups, but in this case, Ir−CH_3 interacts with both "upper" and "lower" pairs of *tert*-butyls and also with hydride, thus confirming a trans Ar−Ir−CH_3 and cis H−Ir−CH_3 arrangement (with the methyl group lying in the plane of the benzene ring). In the nondecoupled ^{13}C NMR spectrum, the carbonyl signal displayed a large $^1H,^{13}C$ coupling constant of ca. 45 Hz, thus indicating that the carbonyl and hydride ligands are arranged in a trans configuration.[24]

The IR spectrum of **7** in hexane reveals a strong ν(CO) band at 1997 cm^{-1} and a very weak band of Ir−H stretch at 2046 cm^{-1} (Figure 1a). This assignment is confirmed by the Raman

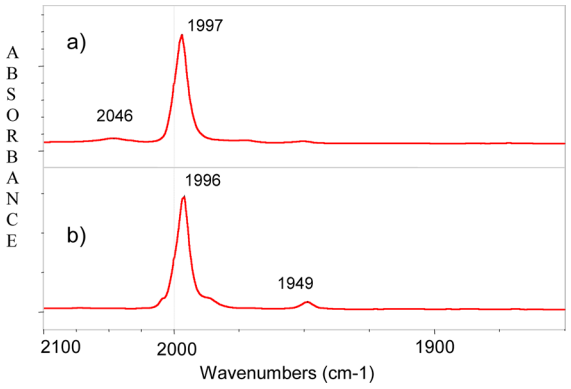


Figure 1. IR spectra of a hexane solution of **7** (a) and its deuterated analogue (b).

spectrum of solid **7**, where in this region two bands with virtually the same frequencies but opposite intensities are observed. For its isomer **8**, along with the ν(CO) band of residual **7**, two overlapping intense bands at 1972 and 1981 cm^{-1} are observed in the IR spectrum of a hexane solution (Figure 2a). In addition, the band at 1949 cm^{-1} is always present associated with the carbonyl complex **4**. In the Raman spectrum of solid **8**, the bands at 1976 and 1983 cm^{-1} are also present, but the intensity ratio is opposite to that observed in the IR spectrum. While the IR spectrum of **7** is typical of a transition-metal complex containing CO and hydride ligands (strong ν(CO) and weak ν(Ir−H)), the pattern in this region

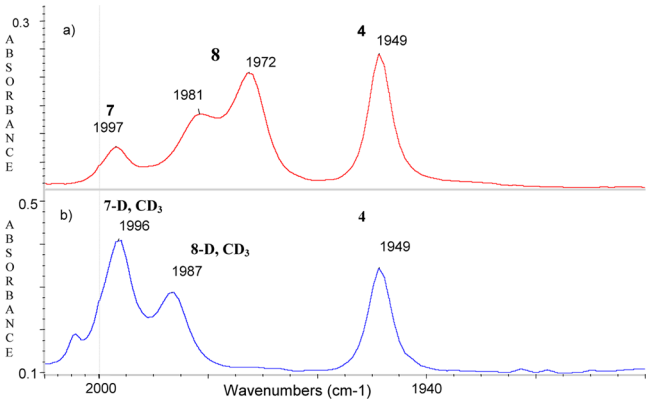
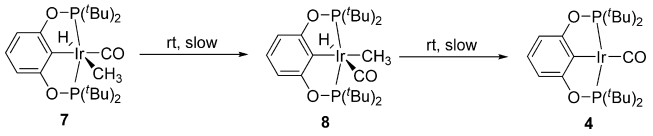


Figure 2. IR spectra of a hexane solution of **8** (a) and its deuterated analogue (b).

for complex **8** indicates a strong coupling of ν(CO) and ν(Ir−H) modes leading to the redistribution of band intensities, which was earlier observed for the trans arrangement of CO and H ligands.[29] Upon deuteration of the hydride position of **7** (Figure 1b), the band at 2046 cm^{-1} is shifted to the low-frequency range. confirming its Ir−H nature with the ν(CO) band being virtually unchanged, while deuteration of **8** results in the disappearance of both intense ν(CO) and ν(Ir−H) bands. This happens because the M−H stretch moves to the low-frequency region, violating the conditions for coupling, and a new absorption at 1987 cm^{-1} appears corresponding to the uncoupled C−O stretch (Figure 2b).

When a solution of complex **7** is kept at room temperature, **7** slowly isomerizes to **8**, where the methyl group and the hydride are in the cis configuration, and **8** slowly loses methane to form carbonyl complex **4** (Scheme 2). These two processes proceed

Scheme 2. Transformations of Complex 7: Rearrangement to 8 Followed by Methane Loss To Give 4



with comparable rates (Figure 3); therefore, it is impossible to obtain a pure sample of **8**, and it was characterized in mixtures with **7** or **4**. The kinetic curves of the tranformations are satisfactorily described by a scheme involving the two consecutive irreversible first-order reactions **7** → **8** → **4**. The assumption that the elimination of methane is a true first-order reaction seems realistic, while the isomerization of **7** to **8** is rather a pseudo-first-order process actually involving several stages. The extracted rate constants $k_{1,obs}$ = 0.0046 ± 0.0001 h^{-1} and k_2 = 0.0033 ± 0.0001 h^{-1} correspond to almost equal activation free energies of 25.5 ± 0.1 and 25.7 ± 0.1 kcal/mol, respectively, at room temperature.

How does the rearrangement of **7** to **8** occur? Both CO and phosphine "arms" are fairly strongly bound to the iridium (we are unaware of examples where bis(phosphinite) iridium pincer complexes lose these ligands, even under harsh conditions of alkane dehydrogenation), for this reason, any kind of dissociative mechanism does not seem likely under mild conditions employed. For the related isomerization of *cis*-Ir(H)$_2$CO[2,6-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$] to *trans*-Ir(H)$_2$CO[2,6-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$],[30] a nondissociative trigonal twist mecha-

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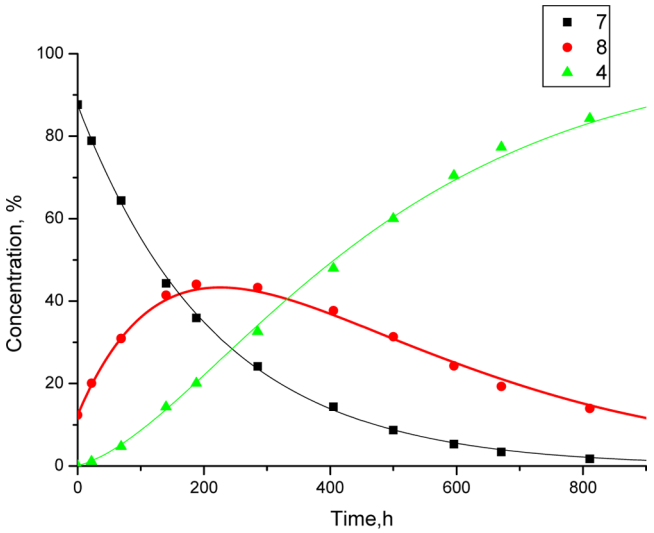


Figure 3. $^{31}P\{^{1}H\}$ NMR monitoring of the rearrangement of **7** to **8** and formation of **4**. Dots correspond to the experimental points and continuous lines to the simulated curves.

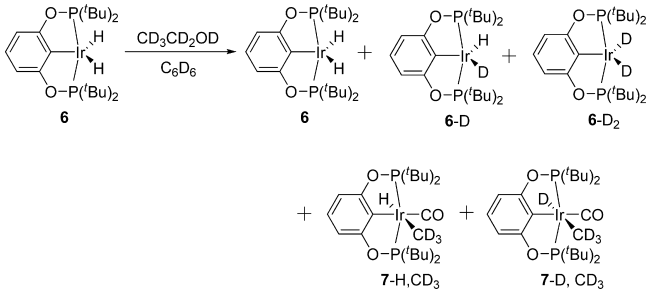
nism was calculated[31] to be the favored one. It should be noted that in calculations the ^{i}Pr groups were replaced by hydrogen atoms. In our case, given the higher degree of steric crowding at the iridium atom (^{t}Bu instead of ^{i}Pr, CH_3 instead of H), such a twist does not seem likely; reversible insertion of CO into the Ir−CH_3 bond followed by rotation of the acetyl group and deinsertion of CO look more realistic. It should be noted that the related isomerization of the isonitrile complex IrH(CNR)-Me[2,6-($^{t}Bu_2PCH_2$)$_2C_6H_3$] to IrH(Me)CNR[2,6-($^{t}Bu_2PCH_2$)$_2C_6H_3$] was reported; however, the mechanism was not discussed.[32]

Decarbonylation of alcohols by iridium pincer complexes is not a common case;[14b,17e,19f,g] formation of methyl hydrido carbonyl complexes from ethanol is even more rare, with only two examples reported,[19g,33] both on iridium compounds. Since a deeper understanding of alcohol decarbonylation at metal centers may be relevant to a range of catalytic processes, it was in our interest to investigate the formation of **7** and **8** in detail.

Iridium pincer complexes which were used for catalytic alkane dehydrogenation (including those used in this work) have been shown to operate via a dissociative 16e−14e mechanism.[21] In the first step, hydrogen from [Ir]H_2 ([Ir] = Ir[2,6-($^{t}Bu_2PCH_2$)$_2C_6H_3$], Ir[2,6-($^{t}Bu_2PO$)$_2C_6H_3$]) is transferred to a sacrificial hydrogen acceptor or removed thermolytically to give the reactive 14e species [Ir]. The latter undergoes oxidative addition of a C−H bond, and subsequent β-hydride elimination produces the olefin product and regenerates [Ir]H_2. This is not the case for dehydrogenation of alcohols by the systems studied. Thus, dihydride complex **6**, which is the particle actually involved in the catalytic cycle, was shown to be thermally stable up to 200 °C[3f,g,21] and does not lose hydrogen readily. Apparently, alcohol assistance is required for this process to proceed at room temperature. Some possible pathways for the first steps of this reaction include (a) coordination of alcohol to **6** followed by hydrogen loss, (b) oxidative addition of the O−H bond of alcohol to give an Ir(V) complex with subsequent reductive elimination, and (c) protonation of hydride with alcohol acting as a Brønsted acid (Scheme 3).

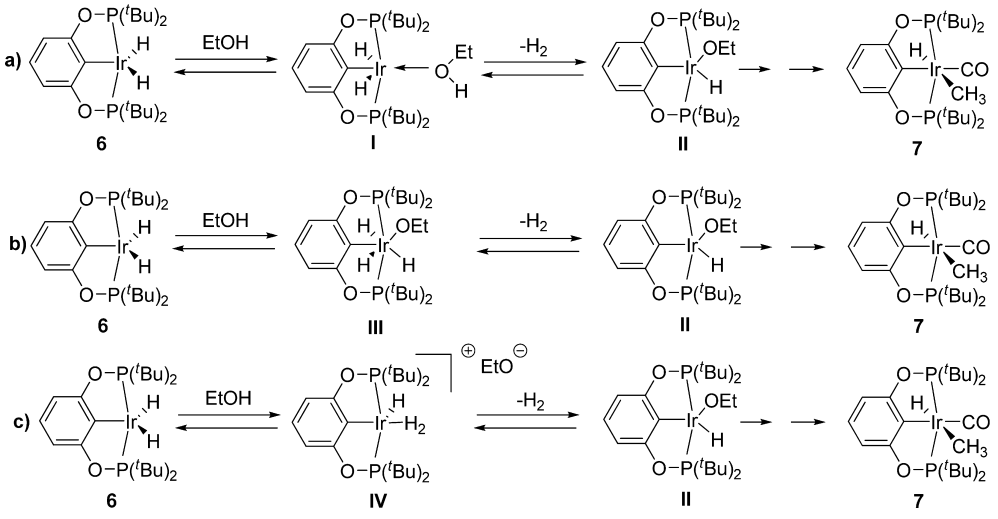
In attempt to clarify this question, the reaction of **6** with C_2D_5OD was conducted, which led to deuterium scrambling and formation of a mixture of **6**, **6-D**, **6-D$_2$**, **7-H,CD$_3$** and **7-D,CD$_3$** (Scheme 4).

Scheme 4. Reaction of 6 with C_2D_5OD



Deuterium exchange at the hydridic positions of **6** was found to be much more facile than the formation of **7**, with deuterium being incorporated from the O−D group. For example, the reaction of **6** with a ca. 8-fold excess of C_2D_5OD approaches the equilibrium point with respect to deuterium distribution

Scheme 3. Possible Pathways of the Reaction of 6 with EtOH



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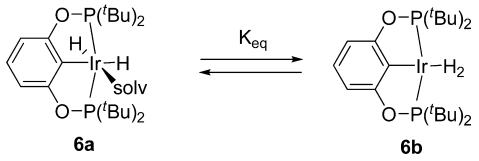
within 4 min (ca. 77% of total deuteration of the hydridic positions was observed with only trace amounts of **7-D,CD$_3$**). It is obvious that pathway (a) cannot explain deuterium scrambling and should be discarded, while the choice between pathways (b) and (c) is ambiguous. In this respect, it is of interest to perform the reaction of **6** with a substrate which would hamper the formation of an analogue of the overcrowded Ir(V) intermediate **III**, such as ^{t}BuOD. This bulky alcohol is not able to enter the coordination sphere of the Ir atom. If the IrH(O^tBu)[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$] particle (analogue of **II**) was formed, it would be stable due to the absence of β-hydrogen and certainly detected by NMR (for example, IrH$_2$[2,6-(^{t}Bu$_2$PCH$_2$)$_2$C$_6$H$_3$] reacts with PhOH to give stable IrH(OPh)[2,6-(^{t}Bu$_2$PCH$_2$)$_2$C$_6$H$_3$][34]); however, this was not the case. Isotopic exchange with ^{t}BuOD proceeds much more slowly (ca. 7% of total deuteration of the hydridic positions under the same conditions as for the reaction with C$_2$D$_5$OD; on approaching the equilibrium point its rate becomes comparable with deuterium scrambling into phosphorus-bound *tert*-butyl groups) but clearly points to pathway (c) as being the only possible route for this substrate. It should be noted that a hydrido dihydrogen complex similar to **IV** with a noncoordinating counteranion, {IrH(H$_2$)[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$]}{BAr$^f_4$}, was reported in the literature.[35]

It was proved that the protonation of the transition-metal hydride is a multistep process occurring via hydrogen-bonded intermediates and ion pairs;[36] thus, detection of such species would give additional proof for pathway (c). Several NMR and IR spectroscopic techniques have been used to establish the formation of hydrogen-bonded species.[37] In particular, the low-frequency shift of the OH stretching vibration in the IR spectra and high-field shift of the hydride resonance in ^{1}H NMR upon addition of the proton donor are among the reliable indicators of hydrogen-bond formation between a metal hydride and an alcohol.[37] Indeed, when an alcohol is added to a benzene-d_6 or toluene-d_8 solution of **6**, a high-field shift of hydride resonance occurs, being slightly larger for EtOH versus ^{t}BuOH and increasing with the excess of alcohol. The highest value obtained was 0.4 ppm for ca. 50-fold excess of EtOH. Addition of ca. 4 equiv of EtOH to a solution of **6** in toluene-d_8 induces a shift of 0.08 ppm, which turns to 0.36 ppm upon cooling to 213 K. However, the hydridic resonance of complex **6** itself undergoes a significant high-field shift at low temperatures[38] and thus, rather surprisingly, the actual difference between **6** and **6** + EtOH remains near the initial 0.08 ppm within experimental error at all ranges of temperatures screened.

Quantitative interpretation of these data remains elusive, due to the very complex nature of compound **6**. A thorough NMR spectroscopic analysis of the deuterium-labeled isotopomers of **6** and their analogues with substituents in para positions by Heinekey and Brookhart revealed significant temperature- and solvent-dependent isotopic shifts and HD coupling constants.[38] These observations, supported by T_1 measurements, were interpreted by a model involving an equilibrium between the solvated Ir(III) dihydride **6a** with nonequivalent hydride sites and the elongated dihydrogen complex of Ir(I) **6b** (Scheme 5). This equilibrium appeared to be fast on the NMR time scale, even at low temperatures, and only one resonance is present in the hydride region of the ^{1}H NMR spectrum of **6**. While at least for bulky ^{t}BuOH, which is not expected to coordinate to the Ir atom and influence the equilibrium in Scheme 5, the shifts of hydride resonances observed can be clearly attributed

Scheme 5. Equilibrium between Two Forms of Complex 6



to formation of hydrogen bonds, other conclusions would be too speculative.

We conducted special IR experiments aimed at detecting H-bonded species between ^{t}BuOH and dihydride **6**. *tert*-Butyl alcohol was selected as an acid because it is inert to dihydride. Its concentration in hexane solution was 0.04 mol/L. In the IR spectrum in the ν(OH) region (Figure 4a), only the band for

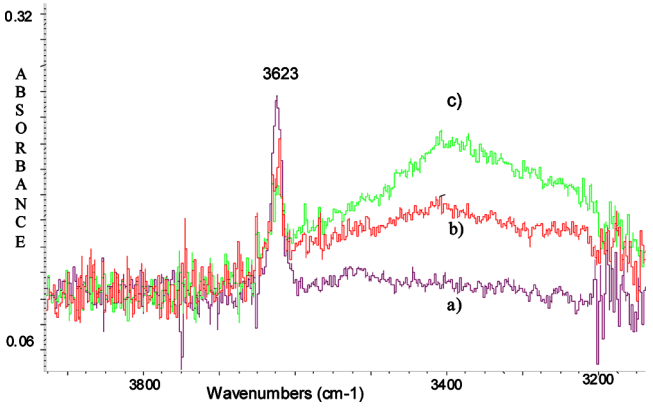


Figure 4. IR spectra in the ν(OH) region in hexane solution: (a) ^{t}BuOH (c = 0.04 M); b) ^{t}BuOH in the same concentration in the presence of **6**; (c) the same mixture as in (b) at 0 °C.

the free OH stretch at 3623 cm^{-1} was observed. When this solution was added to solid **6** (a saturated solution of **6** was obtained, which provided a large excess of the base in the mixture), the intensity of the band at 3623 cm^{-1} decreased and a new broad band with a center of gravity at ca. 3420 cm^{-1} (Figure 4b) appeared in the spectrum. These features (low-frequency shift of the ν(OH) band and intensity growth) are indicative of H-bond formation between dihydride **6** and ^{t}BuOH. Lowering the temperature to 0 °C resulted in a further increase of the intensity of the H-bonded band.

We estimated the H-bond enthalpy from the ν(OH) low-frequency shift value of 203 cm^{-1} using the empirical formula[37a,39]

$$\Delta H^\circ = \frac{18\Delta\nu_{OH}}{\Delta\nu_{OH} + 720}$$

This estimation gave an enthalpy value of about 4 kcal/mol. The basicity factor was estimated using the same ideology[37a,39] by the formula

$$E_j = \frac{\Delta H^\circ_{ij}}{\Delta H^\circ_{11} P_i}$$

where ΔH°_{ij} is the experimental enthalpy and ΔH°_{11} is the value for the pair phenol/diethyl ether taken as a standard (measured in the corresponding solvent; 5.7 kcal/mol for hexane[37a]). For this standard, the basicity and acidity factors are taken as unity. The basicity factor E_j is considered as an objective characteristic of the basic properties of the substance,

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independent of the nature of proton donors and the medium, and can be used for comparison of these properties in a series of related compounds.

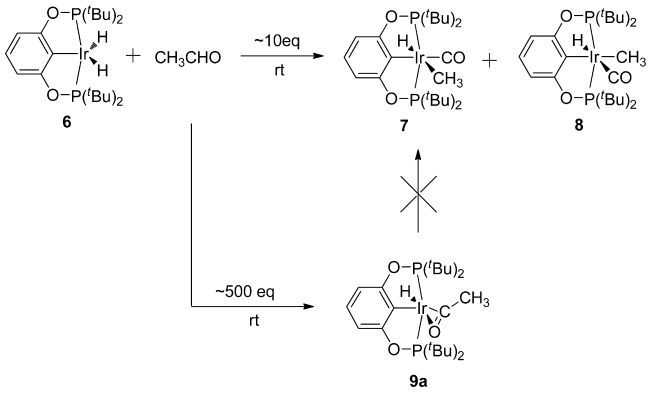
Our estimation of E_j gave a value of 1.23, indicating that dihydride **6** is quite basic and its proton-accepting properties can be compared with those of hydride ligands in $RuH_2[P(CH_2CH_2PPh_2)_3]$ (1.33)[37a] or $CpRuH(CO)PCy_3$ (1.0).[37a]

As for the basic center of H bonding, no distinct evidence could be derived from the IR spectra. We conducted low-temperature IR experiments with a hexane solution of pure dihydride **6**. In the ν(Ir−H) region, dihydride **6** has four bands instead of the two expected for two Ir−H bonds. When the temperature is lowered, the intensity ratio of these bands changes; however, on returning to room temperature, the initial pattern is not restored, thus indicating that in the solution of **6**, complicated processes can occur. For this reason, IR spectra do not provide proof that it is the hydride that is involved in H bonding; however, the high-field shift of the hydride in the ^{1}H NMR points out that it is the most reasonable basic partner for ^{t}BuOH as an acid.

To sum up this part of our research, we presented evidence that the reaction of **6** with alcohols under ambient conditions begins with the formation of hydrogen-bonded species, followed by proton transfer to give the hydrido dihydrogen intermediate **IV** and, presumably, coordination of the counteranion and liberation of dihydrogen to form **II**. However, the contribution of an alternative pathway through the formation of Ir(V) to a reaction with small alcohols cannot be completely excluded.

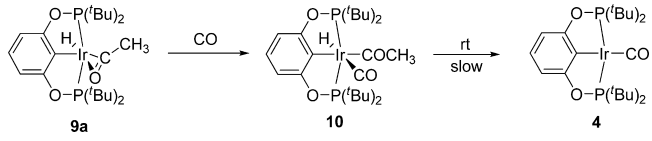
Alcohol decarbonylation is generally believed to proceed through dehydrogenation to give the appropriate carbonyl compounds followed by formation of acyl complexes and migratory deinsertion of CO.[19c,d,g,20] In our case, we have never observed species other than **6** and **7** (and products of its subsequent transformations) in the reaction of **6** with EtOH. To elucidate the further destiny of the putative IrH(OEt)[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$] particle, we performed a reaction of **6** with acetaldehyde. When a slight excess of CH_3CHO was used (~10 equiv), the expected mixture of **7** and **8** was formed within minutes; however, according to the ^{31}P{^{1}H} NMR spectra, it contained a small amount of a new compound. The use of a large excess of CH_3CHO (~500 equiv) resulted in almost selective formation of this new compound, which appeared to be acetyl hydride complex **9a** (Scheme 6). This complex was characterized by NMR and IR spectra and elemental analysis and turned out to be a tricky compound. The ^{31}P{^{1}H} NMR

Scheme 6. Reaction of Dihydride 6 with CH_3CHO



spectrum revealed a singlet at 165.5 ppm, while the hydride appeared as a triplet at −30.38 ppm ($^2J_{P-H}$ = 12.8 Hz) in the ^{1}H NMR spectrum. It should be noted that in the case of iridium pincer complexes, both neutral and cationic, a hydride which is rigorously trans to a vacant coordination site reveals a signal at ca. −40 ppm,[3f,g,40] while a signal near −30 ppm is typical for a hydride which is mutually trans to a low-field ligand, especially oxygen.[28,34,41] Therefore, the presence of the η^2-acetyl group in **9a** may be suggested. In the IR spectrum, we observed a band at 1546 cm^{-1} assigned to an acetyl C−O stretch. This frequency is lower than that typically observed for terminal Ir acyls[42] (near 1600 cm^{-1}) and falls in the range observed for complexes with η^2-acyls.[43] Low-field (>200 ppm) signals are usually observed in ^{13}C NMR spectra for terminal acyls bound to transition metals,[44] especially for those demonstrating low C−O stretching frequencies of the acyl groups, due to the contribution of M$^+$=C(O$^-$)R structures.[45] Nevertheless, the signal of the CH_3CO group is observed at 183.4 ppm, indicating that complex **9a** does not have any significant carbene character. It is remarkable that **9a** does not demonstrate any trend to isomerization to **7** or **8**. Thus, **9a** is stable at ambient temperature, while heating a solution of **9a** in C_6D_6 for 9 h at 80 °C results in decomposition of ca. 5% of **9a** to give **4**. Complex **9a** readily adds CO to form compound **10** (Scheme 7). In the ^{31}P{^{1}H} NMR spectrum, complex **10**

Scheme 7. Addition of CO to Complex 9a



resonates at 161.7 ppm. In the ^{1}H NMR spectrum, the hydride signal appears as a triplet at −8.31 ppm ($^2J_{P-H}$ = 16.7 Hz). The ^{13}C NMR spectrum reveals a singlet at 176.2 ppm corresponding to CH_3CO and a triplet at 182.4 ppm ($^2J_{C-P}$ = 5.0 Hz) from carbonyl. A strong absorption at 2035 cm^{-1} is clearly attributable to the CO ligand, and another strong band at 1590 cm^{-1} corresponds to the acetyl C−O stretch. Also, there is a weak absorption at 2200 cm^{-1} from the Ir−H stretch. The configuration of **10** was confirmed by preparing a ^{13}CO-enriched sample, which demonstrated a large ^{1}H,^{13}C coupling constant of 52.4 Hz indicative of a trans configuration of carbonyl and hydride ligands.[24] Complex **10** slowly decomposes at room temperature to give **4** and acetaldehyde. The same trends were observed for the reaction with propionaldehyde (see Experimental Section). It is worth noting that in this case only the analogue of **8**, namely complex **11**, where H and C_2H_5 are in a cis arrangement (on the basis of a very close chemical shift in ^{31}P{^{1}H} NMR spectrum), was selectively formed when small quantities of aldehyde were used, presumably due to steric reasons.

To summarize, the reaction with CH_3CHO suggests that, surprisingly, acetyl hydrido complex **9a** is not an intermediate on the way from **6** to **7**. As the use of small quantities of CH_3CHO leads to the formation of **7**, it is likely that acetaldehyde is actually involved in the sequence of reactions of **6** with EtOH and is formed upon β-hydride elimination of the Ir(H)OEt particle. Direct addition of the C−C bond of CH_3CHO to Ir is unlikely (no precedents for Ir pincers are known), and thus it may be suggested that two different

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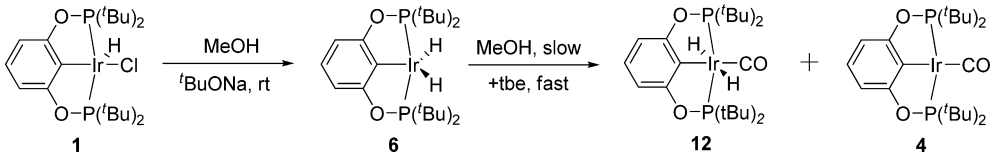
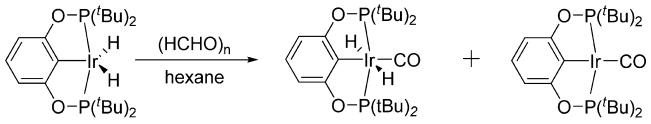
Scheme 8. Decarbonylation of MeOH by Complex 1



isomers (rotamers) of acetyl hydrido complex are formed when **6** reacts with CH_3CHO, depending on the concentration of the latter. One rotamer, **9b**, is able to isomerize to **7**, while for the other, complex **9a**, this possibility is blocked by coordination of oxygen to Ir and/or the necessity of rotation hindered by bulky *tert*-butyl groups. The reaction of CH_3CHO with **6** probably proceeds via an associative mechanism, as was the case for EtOH. However, aldehyde is a much weaker acid compared to alcohol and therefore the mechanisms involving coordination of aldehyde as a Lewis base (similar to pathway (a)) or formation of an Ir(V) intermediate (similar to pathway (b)) seem more probable than protonation.

Decarbonylation of Other Alcohols. Decarbonylation of methanol proceeds in the way similar to that of EtOH. Thus, reaction of **1** with MeOH and ^{t}BuONa in the presence of tbe produces a mixture of trans dihydride **12**[46] and carbonyl complex **4** in a 75:25 ratio after 30 min (Scheme 8). Presumably, this reaction lacks the stereoselectivity observed for formation of **7**, because **12** is stable enough under these conditions to exclude its decomposition to give **4**. Thus, the presence of **4** may be a result of formation of unobserved cis dihydride which loses dihydrogen to give **4**. In contrast to CH_3CHO, paraformaldehyde gives a mixture of **12** and **4** when reacted with **6** rather than hydrido formyl complex (Scheme 9).

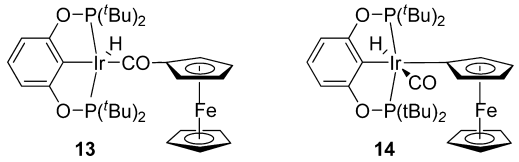
Scheme 9. Reaction of Dihydride 6 with Paraformaldehyde



This result can be ascribed to the poor solubility of paraformaldehyde in hexane, in view of the huge excess of CH_3CHO required for the formation of **9a**. Complex **12** was characterized by NMR and IR spectra. It displays a singlet at 183.5 ppm in $^{31}P\{^1H\}$ NMR and a triplet at −9.48 ppm ($^2J_{P-H}$ = 15.2 Hz) in its ^1H NMR spectrum. The IR spectrum in C_6D_6 reveals an intense absorption at 1995 cm^{-1} corresponding to CO and a weaker band at 1827 cm^{-1} which is characteristic of mutually trans hydride ligands.[19f,30]

Bearing in mind the steric crowding at the iridium atom in **1**, we attempted to use sterically hindered primary alcohols in effort to avoid decarbonylation. We supposed that for bulky substrates the cleavage of a C−C bond to form compounds analogous to **7** and **8** would be inhibited. Indeed, the use of ferrocenylmethanol afforded some aldehyde but did not prevent decarbonylation at all (Scheme 10). Three unstable intermediates were observed by NMR spectroscopy during this reaction. They tend to decompose during chromatography, and all our attempts to separate them by crystallization failed; the thermal stability of these species is sufficiently lower than that of **7** and **8**, and after several days at room temperature complex **4** is the only substance in the reaction mixture observed by $^{31}P\{^1H\}$ NMR. The first intermediate can be obtained in a mixture with formylferrocene by the reaction of **1** with ferrocenylmethanol in the presence of tbe. It reveals a singlet at 183.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum and a triplet ($^2J_{PH}$ = 14.2 Hz) at −36.97 ppm in the ^1H NMR spectrum; this spectrum is consistent with structure **13** (Chart 2), where, in

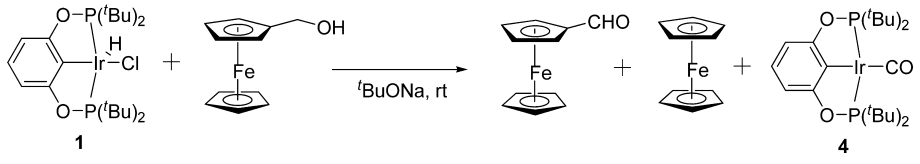
Chart 2. Proposed Intermediates for Ferrocenylmethanol Decarbonylation by Complex 1



contrast to complex **9a**, oxygen is not coordinated to the Ir atom. In the IR spectrum in C_6H_6, the band at 1666 cm^{-1} was ascribed to the ketone ν(CO) in **13**; also, an absorption at 1685 cm^{-1} from formylferrocene was observed. Thus, **13** may be an analogue of the unobserved rotamer of the acetyl hydrido complex, which is responsible for the formation of **7**. Upon standing, a new peak at 161.9 ppm in the $^{31}P\{^1H\}$ NMR spectrum appears (along with the peak from **4**), which corresponds to the hydride signal at −9.65 ppm (t, $^2J_{PH}$ = 17.7 Hz). These values are close to those of **8**; thus, the structure **14** (Chart 2) where H is mutually cis to the ferrocenyl group was proposed for this compound. Finally, at high conversions small amounts of the third intermediate can be detected, which resonates at 184.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum and has a hydride signal at −12.29 ppm (t, $^2J_{PH}$ = 21.4 Hz). These data suggest that it is a six-coordinate Ir(III) complex, for which the P−H coupling of 21.4 Hz is larger than that typically observed for related iridium pincers, indicating significant structural perturbations.

In general, the ruthenocene-based complex **3** demonstrates similar behavior in its reactions with primary alcohols. Thus, it decarbonylates ethanol with formation of the methyl hydrido

Scheme 10. Decarbonylation of Ferrocenylmethanol by Complex 1



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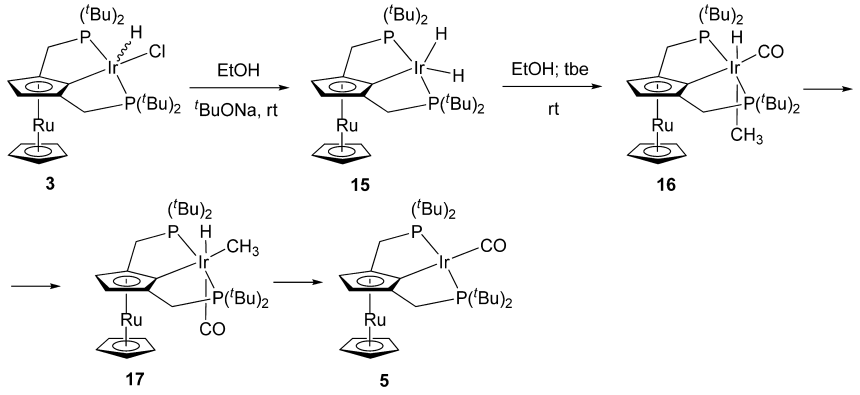
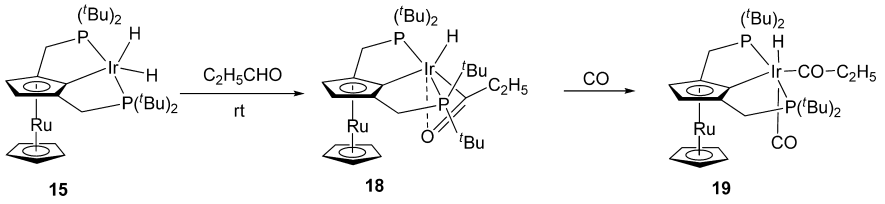
Scheme 11. Decarbonylation of EtOH by Ruthenocene-Based Complex 3



Scheme 12. Reaction of Dihydride 15 with C_2H_5CHO



carbonyl **16**, which further transforms into isomer **17** and carbonyl complex **5** (Scheme 11). This reaction is slower than in the case of **1**, and even in the presence of tbe, it requires several days for the initially formed dihydride **15**[3h] to transform into **16**. Spectral features of **16** and **17** are similar to those of their benzene-based counterparts and are not discussed in detail (see Experimental Section).

The reaction of dihydride **15** with a large excess of C_2H_5CHO leads to the formation of propionyl hydride complex **18**, which resembles benzene-based complex **9a** (Scheme 12). Remarkably, only one of the two possible stereoisomers is formed; the configuration of **18** was confirmed by a NOESY spectrum. Complex **18** adds CO to give the 18e adduct **19**. The arrangement of the ligands in **19** was confirmed by preparing a ^{13}CO-enriched sample, which demonstrated a large $^{1}H,^{13}C$ coupling constant of 52.4 Hz, indicative of a mutually trans arrangement of carbonyl and hydride ligands.[24]

DISCUSSION

Decarbonylation of Alcohols. It is of interest to compare our results with the literature data. The known examples of formation of carbonyl hydrido methyl complexes include generation of $[IrH(CO)(CH_3)Cyttp]BPh_4$ (Cyttp = C_6H_5P-$(CH_2CH_2CH_2PCy_2)_2$) by metalation of the Cyttp ligand in the presence of ethanol[32] and reaction of $IrH_2\{N[2\text{-}(^iPr_2P)\text{-}4\text{-}MeC_6H_3]_2\}$ with ethanol in the presence of norbornene with formation of the $[Ir](H)(CO)CH_3$ complex (H is trans to CH_3), which undergoes photolytically induced reductive elimination of methane to generate an Ir−CO adduct.[19g] In the latter case, some mechanistic details were provided. The proposed mechanism includes generation of the Ir(I) particle $Ir\{N[2\text{-}(^iPr_2P)\text{-}4\text{-}MeC_6H_3]_2\}$ followed by oxidative addition of the O−H bond of the alcohol. Further steps presumably consist of β-hydride elimination to give acetaldehyde and $IrH_2\{N[2\text{-}(^iPr_2P)\text{-}4\text{-}MeC_6H_3]_2\}$ with subsequent reaction between these species accompanied by evolution of hydrogen and formation of the $[Ir](H)(CO)CH_3$ complex. Indeed, the reaction between $[Ir]H_2$ and CH_3CHO was shown to give $[Ir](H)(CO)CH_3$; no formation of hydrido acyl compounds was detected. Irradiation is required to drive reductive elimination of methane, presumably resulting in the formation of the cis isomer.

Decarbonylation of methanol was reported for two iridium pincer complexes. Thus, the $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$ pincer complex promotes methanol decarbonylation in the presence of tbe to generate the corresponding Ir−CO complex,[14b] while the treatment of $\{IrH(C_6H_5)[2,6\text{-}(^tBu_2PCH_2)_2C_5H_3N]\}PF_6$ with methanol upon heating results in stereoselective formation of the trans $[Ir](H)_2CO$.[19f] For the latter reaction, the suggested mechanism involves reductive elimination of benzene and oxidative addition of the O−H bond followed by β-hydride elimination, leading to formaldehyde and the dihydride complex $\{IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_5H_3N]\}PF_6$. In the final step, the aldehyde activation is followed by deinsertion of CO (migration of the hydride) to produce specifically the trans dihydride complex. This last step of the reaction is intriguing, as it appears to be a stereoselective migration resulting in the formation of the trans rather than the cis dihydride complex. The formation of Ir(I) carbonyl in the case of $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$ implies that the migratory deinsertion proceeds stereospecifically to the cis dihydride isomer, since reductive elimination of H_2 to generate the iridium(I) carbonyl must occur from the cis dihydride. Remarkably, $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$ is compatible with primary alcohols other than CH_3OH even at elevated temperatures and is able to catalyze dehydrogenation with formation of aldehydes. This probably results from the high barrier for decarbonylation caused by steric reasons, as CO bonding energies to the model particles $Ir[2,6\text{-}(Me_2PCH_2)_2C_6H_3]$ and $Ir[2,6\text{-}(Me_2PO)_2C_6H_3]$ were calculated to be quite similar (62.2 vs 63.1 kcal/mol),[3c] indicating an almost equal affinity of the catalysts for CO. In our case, presumably both cis and trans dihydrides are formed in the reaction of **1** with methanol, with the unobserved cis isomer immediately decomposing to carbonyl **4**. It is worth noting that

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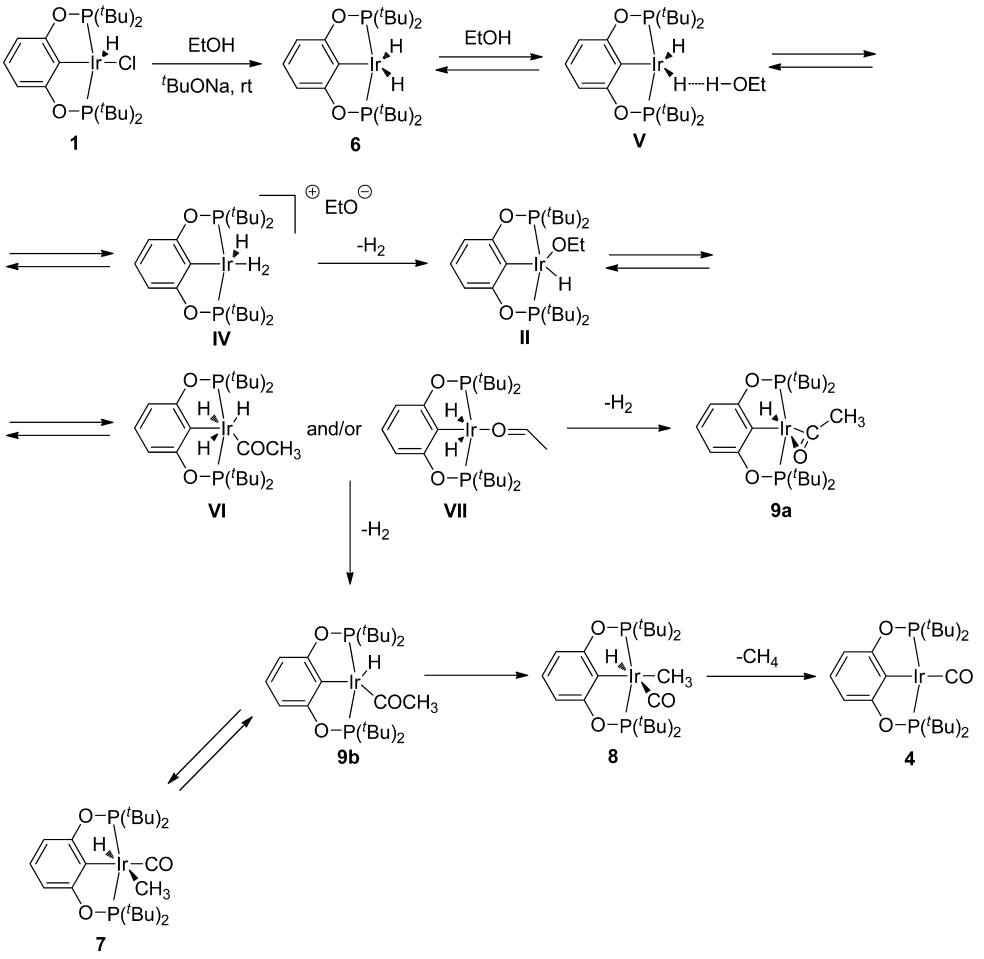
Scheme 13. Proposed Overall Mechanism for EtOH Decarbonylation by Complex 1



better selectivity is observed for ethanol, where trans complex **7** is formed almost exclusively. In this respect, it is interesting that the cis dihydride $Ir(H)_2CO[2,6\text{-}(^iPr_2PCH_2)_2C_6H_3]$ isomerizes to the more stable trans dihydride $Ir(H)_2CO[2,6\text{-}(^iPr_2PCH_2)_2C_6H_3]$ upon heating,[31] while trans complex **7** appears to be less stable than cis complex **8** (presumably for steric reasons). Such different behaviors of related compounds toward alcohols point out the importance of steric factor and potentially open the possibility of impeding the formation of intermediates leading to decarbonylation.

The proposed overall mechanism for decarbonylation of EtOH by **1** is depicted in Scheme 13. Presumably, dehydrochlorination of **1** leads to the formation of the active 14e particle, which oxidatively adds the O−H bond of EtOH followed by β-hydride elimination to give complex **6**. The 1 equiv of CH_3CHO formed might undergo rapid condensation catalyzed by excess base. This is confirmed by the reaction with ferrocenylmethanol, where the corresponding aldehyde is not able to undergo condensations due to the absence of α-hydrogens and remains in the reaction mixture. The further steps are of special interest because they may be relevant to the catalytic cycle of acceptorless dehydrogenation. Complex **6** reacts with EtOH to give hydrogen-bonded intermediate **V**, which after proton transfer affords the cationic complex **IV**. As was proved by deuterium exchange experiments, these stages are reversible and rapid. The next step involving dihydrogen dissociation from **IV** is slow and may be rate determining on the way to **7**. It should be noted that the analogue of **IV**, namely the complex $\{IrH(H_2)[2,6\text{-}(^tBu_2PO)_2C_6H_3]\}\{BAr^f{}_4\}$, is relatively stable and sustains mild heating.[36] β-Hydride elimination from **II** leads to complex **6** and CH_3CHO, which presumably does not leave the coordination sphere of iridium and undergoes further reaction before reacting with the base, forming adduct **VI** and/or **VII**. It is possible that both are formed depending on the aldehyde concentration, with one of them being responsible for the formation of complex **9a** and the other for the unobserved intermediate **9b**. Migratory deinsertion of CO might give complex **7** as the kinetic product and complex **8** as the thermodynamic product.

Comparison among the Various Catalysts. Complexes $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$, **6**, and **15** are well-known catalysts for alkane dehydrogenation. Complex **6** is approximately by 1 order of magnitude more active than its bis(phosphine) counterpart $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$. This difference is primarily attributable to the fact that the metal center of **6** is much less sterically hindered than that of $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$.[3h,21] Complex **15** is slightly more active than **6**, presumably due to a combination of electronic and steric factors. Indeed, the geometry of the ligands around iridium for **15** (P−Ir−P angle, conformation of chelating metallacycles) is rather close to that of **6**, while the electronic properties of pincer ligand in **15** resemble those of $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$.[3h,47] As expected, in the case of alcohols complex **6** outperformed its counterpart $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$. Thus, the quantitative yield with a TON of 7 was reported for dehydrogenation of secondary alcohols by

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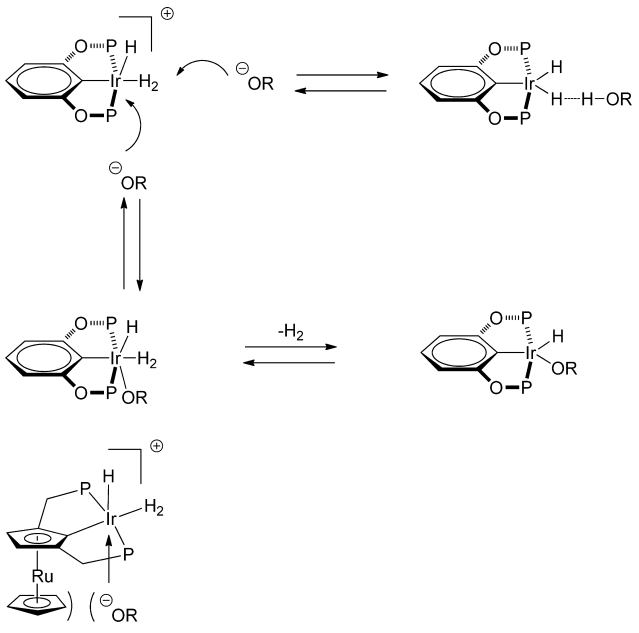
$IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$ in the presence of tbe,[14b] while **6** under similar conditions demonstrated TON values as high as 4000. Remarkably, the attempts to conduct acceptorless dehydrogenation of alcohols using $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$ failed.

The superiority of **15** over **6** was not reproduced for alcohol dehydrogenation; moreover, under any conditions employed **15** showed significantly poorer results.

To rationalize such a behavior of the catalysts, it is necessary to know the mechanism that is operating. It was found that, in the case of EtOH and complex **6**, the mechanism is clearly associative and involves proton transfer from the alcohol. It seems reasonable that, for secondary alcohols, at room temperature the mechanism is the same. However, since at some steps of the associative mechanism the entropy change should be negative (formation of one molecule from two), it is possible that under optimum conditions (near 190 °C) the contribution of the dissosiative 16e−14e mechanism may be significant or even predominating. In any event, the primary reason for the difference in catalytic activity seems to be steric, as it was for alkane dehydrogenation. Moreover, if the proposed mechanism is the one actually operating at elevated temperatures, some peculiar features should be considered. Thus, dissociation of dihydrogen from a cationic complex is expected to be the rate-determining step. As was mentioned earlier, such compounds with non-nucleophilic counteranions are relatively stable and the assistance of an alkoxide anion may be required to accelerate dihydrogen evolution. It is obvious from simple geometrical considerations that a front attack of the alkoxide anion will result in deprotonation, while a bottom attack on the Ir atom may result in nucleophilic assistance (Scheme 14). This bottom attack can be hindered by the unsubstituted cyclopentadienyl ring for **15** and unsuitable arrangement of the *tert*-butyl groups in $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$. In addition, increased electron density on the Ir atom[47] for **15** and $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$ in comparison to that for **6** may result in stronger hydrogen binding.

Scheme 14. Proposed Interactions of Cationic Hydrido Dihydrogen Intermediates with Alkoxide Counteranion: Deprotonation or Coordination



The comparison of our results with other catalysts for alcohol dehydrogenation is not straightforward, because there is no benchmark reaction and several characteristics of the catalyst should be considered. Thus, on the one hand, the state-of-the-art catalysts for acceptorless alcohol dehydrogenation significantly outperform the complexes reported here with respect to turnover frequencies and total turnover numbers. The best examples developed by Beller and co-workers include a mixture of $[RuCl_2(p\text{-cymene})]_2$ and tetramethylethylenediamine[16f] and a mixture of $HN(CH_2CH_2P^iPr_2)_2$ and $RuH_2(PPh_3)_3CO$,[16k] which showed 17215 TON after 11 days and an impressive 40000 TON after 12 h, correspondingly, in the dehydrogenation of ^{i}PrOH at 90 °C. However, taking into consideration 4 ppm catalyst loading, these results correspond to conversions of only 7% and 16%, respectively. On the other hand, a dibenzobarrelene iridium pincer complex developed by Gelman and co-workers[17e] and a Cp*Ir complex with a hydroxypyridine-based C,N chelating ligand introduced by Fujita and Yamaguchi[17f] provide excellent conversions (for example, for $PhCH(OH)CH_3$ 94%, 940 TON, solution in *p*-xylene, reflux, 6 h, and 96%, 960 TON, solution in *p*-xylene, reflux, 20 h, respectively) with moderate TON. Performance of the most active catalyst reported here, complex **2** (85% conversion, 3420 TON, 190 °C, 32 h, neat $PhCH(OH)CH_3$) is roughly comparable to those of the last two systems concerning conversion and TON. Higher temperatures are required for **2**, while it takes advantage of carrying out catalysis in neat substrate instead of organic solvent.

■ CONCLUSION

The reactivity of three iridium pincer complexes toward alcohols has been reported. Bis(phosphinite) complex **1** demonstrated good catalytic activity for the dehydrogenation of secondary alcohols, both with and without a sacrificial hydrogen acceptor. Mechanistic investigations showed that dihydride **6** is the particle actually involved in the catalytic cycle. Remarkably, dehydrogenation with **6** can be carried out under basic, neutral, and acidic conditions, depending on the catalyst precursor (**1**, **6**, or **2**); the last appeared to be the preferable choice presumably due to suppression of out-of-cycle species formation. Thus, the activity of **2** in acceptorless alcohol dehydrogenation is comparable to that of the state-of-the art catalysts with respect to the combination of conversion and TON, though higher temperatures are required for **2** to achieve satisfactory performance.

In the case of primary alcohols, rapid decarbonylation leads to the formation of catalytically inactive species. A detailed study of reaction of **1** with EtOH allowed us to trace the unprecedented sequence of rearrangements on the way from **1** to **4** and to gain some insight into the factors influencing the reactivity of Ir pincers with alcohols. Steric factors appeared to be of primary importance and are responsible for a fine balance between a number of possible reaction pathways; thus, the more open geometry of complex **6** in comparison to that of $IrH_2[2,6\text{-}(^tBu_2PCH_2)_2C_6H_3]$ results in a significantly improved reactivity toward secondary alcohols, while for the same reason **6** is not compatible with primary alcohols due to a lower barrier to decarbonylation.

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EXPERIMENTAL SECTION

General Considerations. All manipulations were conducted under an argon atmosphere using standard Schlenk techniques unless otherwise stated. All solvents (including deuterated) were distilled under an argon atmosphere from the appropriate drying agents. Commercially available reagents were used as received. C_2D_5OD contained ca. 90% atom D, while ^{t}BuOD contained 96%. Compounds **1**,[3f] **3**,[3h] and **6**[3g] were prepared according to the literature procedures. NMR spectra were recorded on Bruker Avance 400 and 600 MHz spectrometers. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are reported in parts per million downfield from tetramethylsilane; the residual signals of deuterated solvents were used as references (7.26 ppm for $CDCl_3$, 7.16 ppm for C_6D_6). In ^{13}C{^{1}H} NMR measurements the signals of C_6D_6 (128.1 ppm) and $CDCl_3$ (77.2) were used as a reference. Some resonances demonstrate additional splitting due to incomplete {^{1}H} decoupling of the hydride signals and thus appear as multiplets rather than virtual triplets. ^{31}P{^{1}H} NMR chemical shifts are reported relative to an external 85% solution of phosphoric acid in D_2O. ^{19}F{^{1}H} NMR chemical shifts are reported relative to external $CFCl_3$. Assignments of signals were confirmed using HMQC, HSQC, and HMBC spectra where necessary. FTIR spectra were recorded on a Nicolet Magna-IR 750 Fourier spectrometer with a resolution of 2 cm^{-1}. Elemental analyses were performed at the A. N. Nesmeyanov Institute of Organoelement Compounds of the RAS.

Synthesis of {IrH(acetone)[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$]}{BF$_4$} (2). Complex **1** (0.058 g, 0.093 mmol) was partially dissolved in 15 mL of acetone in a light-protected Schlenk flask, and a solution of $AgBF_4$ (0.019 g, 0.097 mmol) in 5 mL of acetone was added dropwise. The reaction mixture was stirred for 0.5 h and then kept for several minutes without stirring. The yellow-orange solution was decanted and evaporated, and the residue was recrystallized from an acetone/hexane mixture. After it was washed with hexane and dried under vacuum **2** (0.058 g, 85%) was obtained as an orange powder. Anal. Calcd for $C_{25}H_{46}BF_4IrO_3P_2$: C, 40.82; H, 6.30. Found: C, 40.44; H, 6.42. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 6.81 (t, 1H, $^3J_{HH}$ = 7.9 Hz, H4), 6.54 (d, 2H, $^3J_{HH}$ = 7.9 Hz, H3 and H5), 2.29 (br s, 6H, $(CH_3)_2CO$), 1.36−1.32 (m, 36H, 4 ^{t}Bu), −42.93 (br s, 1H, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$): δ 175.3 (br s). ^{19}F{^{1}H} NMR (376.50 MHz, $CDCl_3$): −151.5 (very br s). IR (KBr, cm^{-1}): 1653 (s), 1637 (s).

Decarbonylation of Ethanol. Formation of IrH(CO)CH$_3$[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$] (7) and IrH(CH$_3$)CO[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$] (8). Complex **1** (0.0159 g, 0.025 mmol) and ^{t}BuONa (0.0085 g, 0.089 mmol) were placed into a J. Young NMR tube, and the ampule was evacuated and refilled with Ar. After this, C_6D_6 (ca. 0.7 mL) and EtOH (0.04 mL, 0.686 mmol) were added via syringe. The ampule was vigorously shaken for several minutes, accompanied by dissolution of **1** and formation of a red solution containing **6** and some quantity of **7**. Then *tert*-butylethylene (0.02 mL, 0.155 mmol) was added, and the ampule was shaken and left for 0.5−1 h. After this period, the reaction was complete and only **7** and **8** in a 98:2 ratio were present, according to NMR. The reaction mixture was evaporated, and the residue was extracted with pentane. The solvent was removed under vacuum to give mixture of **7** and **8** as a yellow powder in almost quantitative yield. Anal. Calcd for $C_{24}H_{43}IrO_3P_2$: C, 45.48; H, 6.84. Found: C, 45.59; H, 6.91.

Characterization of ***7****.* ^{1}H NMR (400.13 MHz, C_6D_6): δ 6.82 (t, 1H, $^3J_{HH}$ = 7.8 Hz, H4), 6.74 (d, 2H, $^3J_{HH}$ = 7.8 Hz, H3 and H5), 1.31 (vt, 18H, J = 7.2 Hz, 2 ^{t}Bu), 1.26 (vt, 18H, J = 7.1 Hz, 2 ^{t}Bu), 0.16 (td, 3H, $^3J_{PH}$ = 3.1 Hz, $^3J_{HH}$ = 1.6 Hz, Ir-CH$_3$), −10.93 (tq, 1H, $^2J_{PH}$ = 18.6 Hz, $^3J_{HH}$ = 1.5 Hz, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 169.4. ^{13}C{^{1}H} NMR (150.93 MHz, C_6D_6) 181.3 (m, Ir-CO), 163.3 (vt, J = 6.0 Hz, C2 and C6), 134.9 (m, C1), 125.5 (s, C4), 105.8 (vt, J = 5.6 Hz, C3 and C5), 43.7 (m, 2 $C(CH_3)_3$), 42.9 (vt, J = 11.6 Hz, 2 $C(CH_3)_3$), 29.2 (vt, J = 2.8 Hz, 2 $C(CH_3)_3$), 28.0 (vt, J = 2.3 Hz, 2 $C(CH_3)_3$), −26.7 (m, Ir-CH$_3$). IR (hexane, cm^{-1}): 2046 (w, Ir−H), 1997 (s, Ir-CO).

Characterization of ***8****.* ^{1}H NMR (400.13 MHz, C_6D_6): δ 6.88 (t, 1H, $^3J_{HH}$ = 7.8 Hz, H4), 6.78 (d, 2H, $^3J_{HH}$ = 7.8 Hz, H3 and H5), 1.33 (vt, 18H, J = 7.4 Hz, 2 ^{t}Bu), 1.22 (vt, 18H, J = 7.2 Hz, 2 ^{t}Bu), 0.62 (td, 3H, $^3J_{PH}$ = 3.8 Hz, $^3J_{HH}$ = 1.5 Hz, Ir-CH$_3$), −9.71 (tq, 1H, $^2J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 1.5 Hz, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 163.7. ^{13}C{^{1}H} NMR (150.93 MHz, C_6D_6): δ 186.0 (m, Ir-CO), 164.2 (vt, J = 4.5 Hz, C2 and C6), 125.9 (s, C4), 123.2 (vt, J = 4.6 Hz, C1), 104.7 (vt, J = 5.2 Hz, C3 and C5), 41.7 (two overlapping vt, J_1 = 12.2 Hz, J_2 = 13.6 Hz, 4 $C(CH_3)_3$), 28.6 (vt, J = 3.0 Hz, 2 $C(CH_3)_3$), 28.5 (vt, J = 2.6 Hz, 2 $C(CH_3)_3$), −47.8 (vt, J = 3.8 Hz, Ir-CH$_3$). IR (hexane, cm^{-1}): 1981 (s), 1972 (s).

Reaction of 6 with Deuterated Alcohols. Formation of 7-D,CD$_3$ and 8-D,CD$_3$. Complex **1** (0.0172 g, 0.027 mmol) and ^{t}BuONa (0.0070 g, 0.073 mmol) were placed into a NMR tube, and the ampule was evacuated and refilled with Ar. Then, C_6D_6 (ca. 0.7 mL) was added via syringe using a rubber septum and hydrogen was bubbled through the reaction mixture via a needle until it became pale orange. A slow flow of Ar was bubbled using the same technique until the reaction mixture became red, indicating the formation of complex **6**. Then, C_2D_5OD (0.50 mL, 0.858 mmol) was added and the ampule was shaken. After ca. 0.5 h, the reaction mixture consisted of an 88:12 mixture of isotopomers of **6** and **7**, where "**6**" consisted of 3% of **6**, 27% of **6-D**, and 70% of **6-D$_2$** while "**7**" contained 10% of **7-H,CD$_3$** and 90% of **7-D,CD$_3$**. After this, *tert*-butylethylene (0.02 mL, 0.155 mmol) was added and **7-D,CD$_3$** and **8-D,CD$_3$** were isolated following the procedure described above in almost quantitative yield. The reactions with other amounts of C_2D_5OD as well as with ^{t}BuOD were conducted in a similar manner.

Reaction of 6 with a Small Excess of CH$_3$CHO with Formation of IrH(CO)CH$_3$[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$] (7) and IrH(CH$_3$)CO[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$] (8). Complex **1** (0.063 g, 0.101 mmol) and ^{t}BuONa (0.031 g, 0.323 mmol) were suspended in 10 mL of hexane in a rubber septum capped Schlenk flask while the flask was purged with hydrogen. The suspension was stirred for several hours under a slow flow of hydrogen until it became pale orange, and then the reaction mixture was filtered through a thin layer of Celite into another Schlenk flask. The stirred solution was purged with Ar until it became red, indicating the formation of complex **6**, and then 1 drop of CH_3CHO was added via syringe. The color changed from red to yellow within several minutes. The solution was stirred for 1 h and then evaporated to dryness, giving a mixture of **7** and **8** (0.054 g, 84%) as a yellow powder.

Reaction of 6 with a Large Excess of CH$_3$CHO with Formation of Ir(H)COCH$_3$[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$] (9a). Complex **1** (0.061 g, 0.098 mmol) and ^{t}BuONa (0.030 g, 0.313 mmol) were suspended in 10 mL of hexane in a rubber septum capped Schlenk flask while the flask was purged with hydrogen. The suspension was stirred for several hours under a slow flow of hydrogen until it became pale orange, and then the reaction mixture was filtered through a thin layer of Celite into another Schlenk flask. The stirred solution was purged with Ar until it became red, indicating the formation of complex **6**, and then CH_3CHO (2 mL, 35 mmol) was added in one portion via syringe. The color changed from red to yellow immediately. The solution was stirred for 10 min and then evaporated to dryness, giving complex **9a** (0.057 g, 92%) as a yellow powder. Anal. Calcd for $C_{24}H_{43}IrO_3P_2$: C, 45.48; H, 6.84. Found: C, 45.41; H, 6.88. ^{1}H NMR (400.13 MHz, C_6D_6): δ 6.78 (t, 1H, $^3J_{HH}$ = 7.8 Hz, H4), 6.69 (d, 2H, $^3J_{HH}$ = 7.8 Hz, H3 and H5), 1.80 (s, 3H, $COCH_3$), 1.40 (vt, 18H, J = 7.0 Hz, 2 ^{t}Bu), 1.30 (vt, 18H, J = 7.3 Hz, 2 ^{t}Bu), −30.38 (t, 1H, $^2J_{PH}$ = 12.8 Hz, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 165.5. ^{13}C{^{1}H} NMR (150.93 MHz, C_6D_6): 181.4 (s, Ir-$COCH_3$), 166.2 (vt, J = 6.0 Hz, C2 and C6), 124.1 (s, C4), 109.5 (m, C1), 104.9 (vt, J = 5.2 Hz, C3 and C5), 42.1 (vt, J = 12.2 Hz, 2 $C(CH_3)_3$), 40.1 (vt, J = 12.1 Hz, 2 $C(CH_3)_3$), 28.5 (vt, J = 3.2 Hz, 2 $C(CH_3)_3$), 27.4 (br s, 2 $C(CH_3)_3$), 25.5 (s, Ir-$COCH_3$). IR ($CHCl_3$, cm^{-1}): 1546 (s, Ir-$COCH_3$).

Synthesis of IrH(COCH$_3$)CO[2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$] (10). Complex **9a** (0.043 g, 0.068 mmol) was dissolved in C_6D_6 (0.6 mL) in a septum-capped NMR tube, and CO was bubbled through the resulting solution via a needle for 30 min accompanied by a color change from yellow to pale yellow. Evaporation of the volatiles gave complex **10** in almost quantitative yield as a pale yellow powder. Anal. Calcd for

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$C_{25}H_{43}IrO_4P_2$: C, 45.37; H, 6.55. Found: C, 45.31; H, 6.38. ^{1}H NMR (400.13 MHz, C_6D_6): δ 6.75 (t, 1H, $^3J_{HH}$ = 7.9 Hz, H4), 6.60 (d, 2H, $^3J_{HH}$ = 7.9 Hz, H3 and H5), 2.26 (s, 3H, $COCH_3$), 1.41 (vt, 18H, J = 7.7 Hz, 2 ^{t}Bu), 1.26 (vt, 18H, J = 7.4 Hz, 2 ^{t}Bu), −8.31 (t, 1H, $^2J_{PH}$ = 16.7 Hz, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 161.7. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6): 182.4 (m, Ir-CO), 176.2 (s, Ir-$COCH_3$), 164.0 (vt, J = 4.3 Hz, C2 and C6), 126.0 (s, C4), 109.0 (vt, J = 2.7 Hz, C1), 105.9 (vt, J = 4.9 Hz, C3 and C5), 42.5 (vt, J = 12.8 Hz, 2 $C(CH_3)_3$), 41.0 (vt, J = 11.7 Hz, 2 $C(CH_3)_3$), 28.5 (vt, J = 3.1 Hz, 2 $C(CH_3)_3$), 27.7 (vt, J = 2.8 Hz, 2 $C(CH_3)_3$), 21.3 (s, Ir-$COCH_3$). IR ($CHCl_3$, cm^{-1}): 2196 (w, Ir−H), 2033 (s, Ir-CO), 1591 (s, Ir-$COCH_3$).

Synthesis of IrH($COCH_3$)CO[2,6-(^{t}Bu_2PO)$_2C_6H_3$] (10) with ^{13}C-Labeled CO. Complex **9a** (0.005 g, 0.008 mmol) was dissolved in C_6D_6 (0.6 mL) in a rubber septum capped NMR tube, and ^{13}CO (86.4 atom % ^{13}C) was slowly bubbled through the resulting solution via a needle for 30 min. A mixture of **10** and **10-^{13}CO** was formed in almost quantitative yield according to NMR. Selected signals for **10-^{13}CO** are as follows. ^{1}H NMR (400 MHz, C_6D_6): −8.29 (dt, 1H, $^2J_{CH}$ = 53.9 Hz, $^2J_{PH}$ = 16.7 Hz, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 161.7. ^{13}C NMR (100.61 MHz, C_6D_6) 182.4 (dt, $^2J_{CH}$ = 53.9 Hz, $^2J_{CP}$ = 6.3 Hz, Ir-CO).

Reaction of 6 with a Small Excess of C_2H_5CHO with Formation of IrH(C_2H_5)CO[2,6-(^{t}Bu_2PO)$_2C_6H_3$] (11). The reaction was conducted in a manner similar to the aforementioned reaction with acetaldehyde. Starting from complex **1** (0.023 g, 0.037 mmol), ^{t}BuONa (0.009 g, 0.094 mmol) and 1 drop of C_2H_5CHO, complex **11** (0.021 g, 87%) was obtained as a yellow powder. Anal. Calcd for $C_{25}H_{45}IrO_3P_2$: C, 46.35; H, 7.00. Found: C, 46.39; H, 7.07. ^{1}H NMR (400.13 MHz, C_6D_6): δ 6.89 (t, 1H, $^3J_{HH}$ = 7.8 Hz, H4), 6.77 (d, 2H, $^3J_{HH}$ = 7.8 Hz, H3 and H5), 2.21 (t, $^3J_{HH}$ = 7.8 Hz, Ir-CH_2CH_3), 1.78 (m, 2H, Ir-CH_2CH_3), 1.35 (vt, 18H, J = 7.3 Hz, 2 ^{t}Bu), 1.22 (vt, 18H, J = 7.2 Hz, 2 ^{t}Bu), −9.57 (tt, 1H, $^2J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 1.4 Hz, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 162.3 IR (hexane, cm^{-1}): 1991 (m), 1981 (s), 1966 (s).

Reaction of 6 with a Large Excess of C_2H_5CHO with Formation of Ir(H)COC_2H_5[2,6-(^{t}Bu_2PO)$_2C_6H_3$]. The reaction was conducted in a manner similar to the aforementioned reaction with acetaldehyde. Starting from complex **1** (0.092 g, 0.147 mmol), ^{t}BuONa (0.045 g, 0.469 mmol), and C_2H_5CHO (2 mL, 28 mmol), complex Ir(H)COC_2H_5[2,6-(^{t}Bu_2PO)$_2C_6H_3$] (0.081 g, 85%) was obtained as a yellow powder. Anal. Calcd for $C_{25}H_{45}IrO_3P_2$: C, 46.35; H, 7.00. Found: C, 46.19; H, 7.09. ^{1}H NMR (400.13 MHz, C_6D_6): δ 6.77 (t, 1H, $^3J_{HH}$ = 7.8 Hz, H4), 6.68 (d, 2H, $^3J_{HH}$ = 7.8 Hz, H3 and H5), 2.18 (q, 2H, $^3J_{CH}$ = 7.6 Hz, $COCH_2CH_3$), 1.38 (vt, 18H, J = 7.0 Hz, 2 ^{t}Bu), 1.29 (vt, 18H, J = 7.2 Hz, 2 ^{t}Bu), 1.12 (t, 3H, $^3J_{CH}$ = 7.6 Hz, $COCH_2CH_3$), −30.43 (t, 1H, $^2J_{PH}$ = 12.7 Hz, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 165.5. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6) 186.4 (s, Ir-$COCH_2CH_3$), 166.2 (vt, J = 6.0 Hz, C2 and C6), 124.1 (s, C4), 109.6 (m, C1), 104.8 (vt, J = 5.4 Hz, C3 and C5), 42.2 (vt, J = 12.2 Hz, 2 $C(CH_3)_3$), 40.1 (vt, J = 12.1 Hz, 2 $C(CH_3)_3$), 32.4 (s, $COCH_2CH_3$), 28.5 (vt, J = 3.4 Hz, 2 $C(CH_3)_3$), 27.4 (vt, J = 2.8 Hz, 2 $C(CH_3)_3$), 9.5 (s, Ir-$COCH_2CH_3$). IR ($CHCl_3$, cm^{-1}): 1536 (s, Ir-$COCH_2CH_3$).

Synthesis of IrH(CO)$COCH_2CH_3$[2,6-(^{t}Bu_2PO)$_2C_6H_3$]. The reaction was conducted in a manner similar to the aforementioned synthesis of **10**. Starting from complex Ir(H)COC_2H_5[2,6-(^{t}Bu_2PO)$_2C_6H_3$] (0.031 g, 0.048 mmol), IrH(COC_2H_5)CO[2,6-(^{t}Bu_2PO)$_2C_6H_3$] was obtained in almost quantitative yield as a pale yellow powder. Anal. Calcd for $C_{26}H_{45}IrO_4P_2$: C, 46.21; H, 6.71. Found: C, 46.09; H, 6.93. ^{1}H NMR (400 MHz, C_6D_6): δ 6.76 (t, 1H, $^3J_{HH}$ = 8.0 Hz, H4), 6.61 (d, 2H, $^3J_{HH}$ = 8.0 Hz, H3 and H5), 2.57 (q, 2H, $^3J_{CH}$ = 7.6 Hz, $COCH_2CH_3$), 1.40 (vt, 18H, J = 7.7 Hz, 2 ^{t}Bu), 1.33 (t, 3H, $^3J_{CH}$ = 7.6 Hz, $COCH_2CH_3$), 1.26 (vt, 18H, J = 7.4 Hz, 2 ^{t}Bu), −8.30 (t, 1H, $^2J_{PH}$ = 16.7 Hz, Ir−H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 161.6. IR ($CHCl_3$, cm^{-1}): 2202 (w, Ir−H), 2032 (s, Ir-CO), 1601 (s, Ir-$COCH_3$).

Kinetics of Thermolysis of 7 and 8. A mixture of **7** and **8** (87.7:12.3; 0.0221 g, 0.035 mmol) was dissolved in C_6D_6 (0.74 mL) in a J. Young NMR tube and kept at room temperature. The ^{31}P{^{1}H} spectra were recorded immediately and after specified intervals (see Figure 3). Alternatively, decomposition can be achieved by placing an NMR tube with solution of **7** and **8** in C_6D_6 into a bath with refluxing EtOH for 3 h. Complex **4** and CH_4 were observed as the only products of decomposition. Ca. 0.125 equiv of CH_4 was present in the solution according to ^{1}H NMR. Taking into consideration the solubility of methane in toluene,[48] it seems reasonable that the rest of methane was present in the gas phase; a similar situation was reported in ref 32.

Thermolysis of 9a. Complex **9a** (0.005 g, 0.008 mmol) was dissolved in C_6D_6 (0.3 mL) in a J. Young NMR tube, and the tube was immersed into a bath with refluxing EtOH. Periodically, the ampule was cooled to room temperature and the NMR spectra were recorded. After 9 h, ca. 5% of complex **9a** decomposed with formation of complex **4**.

Thermolysis of 10. Complex **10** (0.006 g, 0.009 mmol) was dissolved in C_6D_6 (0.3 mL) in a J. Young NMR tube, and the tube was immersed into a bath with refluxing EtOH. Periodically, the ampule was cooled to room temperature and the NMR spectra were recorded. After 1 h, ca. 50% of complex **10** decomposed with formation of complex **4** and acetaldehyde. After 10 h, the reaction was almost complete. The amount of acetaldehyde produced corresponded well with the amount of complex **4**.

Decarbonylation of Methanol. Formation of *trans*-IrH$_2$(CO)-[2,6-(^{t}Bu_2PO)$_2C_6H_3$] (12) and IrCO[2,6-(^{t}Bu_2PO)$_2C_6H_3$] (4). Complex **1** (0.020 g, 0.032 mmol) and ^{t}BuONa (0.010 g, 0.104 mmol) were placed into a NMR tube, and the ampule was evacuated and refilled with Ar. Then, C_6D_6 (ca. 0.7 mL) and MeOH (0.04 mL, 0.998 mmol) were added via syringe using a rubber septum. The ampule was vigorously shaken for several minutes, accompanied by dissolution of **1** and formation of a red solution containing **6** and some quantity of **12**. Then *tert*-butylethylene (0.02 mL, 0.155 mmol) was added, and the ampule was shaken and left for 0.5−1 h. For this time, **12** and **4** in a 75:25 ratio were present, along with trace amounts of a compound with signal at 183.0 ppm in the ^{31}P{^{1}H} NMR assigned to IrD(C_6D_5)[2,6-(^{t}Bu_2PO)$_2C_6H_3$].[3g] ^{1}H NMR (400.13 MHz, C_6D_6): δ 6.83 (t, 1H, $^3J_{HH}$ = 8.0 Hz, H4), 6.72 (d, 2H, $^3J_{HH}$ = 8.0 Hz, H3 and H5), 1.34 (vt, 36H, J = 7.4 Hz, 4 ^{t}Bu), −9.48 (t, 1H, $^2J_{PH}$ = 15.2 Hz, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 183.5. IR (C_6D_6, cm^{-1}): 1995 (s, Ir-CO), 1827 (m, Ir-H).

Reaction of 6 with $(HCHO)_n$. Complex **1** (0.052 g, 0.083 mmol) and ^{t}BuONa (0.027 g, 0.281 mmol) were suspended in 10 mL of hexane in a rubber septum capped Schlenk flask while the flask was purged with hydrogen. The suspension was stirred for several hours under a slow flow of hydrogen until it became pale orange, and then the reaction mixture was filtered through a thin layer of Celite into another Schlenk flask. The stirred solution was purged with Ar until it became red, indicating the formation of complex **6**, and then $(HCHO)_n$ (2.01 g, 67 mmol) was added in one portion. The suspension was stirred for 1 h and then allowed to precipitate. The yellow solution was decanted and filtered through a thin pad of Celite. Evaporation of the volatiles afforded 0.045 g of a mixture of **12** and **4** (ca. 75:25).

Decarbonylation of Ferrocenylmethanol. Complex **1** (0.0095 g, 0.015 mmol), ^{t}BuONa (0.0045 g, 0.047 mmol), and ferrocenylmethanol (0.0164 g, 0.076 mmol) were placed into a NMR tube, and the ampule was evacuated and refilled with Ar. Then, C_6D_6 (ca. 0.7 mL) was added via syringe. The ampule was vigorously shaken for several minutes, and the NMR spectra were recorded periodically. After 10 days, the volatiles were evaporated under vacuum and column chromatography on silica afforded **4**, ferrocene, and formylferrocene (along with nonreacted ferrocenylmethanol) as the major products. The quantity of formylferrocene corresponds to 1.6 TON.

Decarbonylation of Ethanol by 3. Complex **3** (0.016 g, 0.021 mmol) and ^{t}BuONa (0.008 g, 0.083 mmol) were placed into a J. Young NMR tube, and the ampule was evacuated and refilled with Ar. Then, C_6D_6 (ca. 0.4 mL) and EtOH (0.02 mL, 0.343 mmol) were added via syringe. The ampule was vigorously shaken for several minutes, accompanied by dissolution of **3** and formation of a brown-

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red solution containing **15**. Then *tert*-butylethylene (0.02 mL, 0.155 mmol) was added, the ampule was shaken, and the NMR spectra were recorded periodically. After 4 days, consumption of **15** was almost complete and **16** was the main substance present in the system. Further, the formation of **17**, **5**, and small amounts of unidentified compounds was observed.

Characterization of ***16****.* ^{1}H NMR (400.13 MHz, C_6D_6): δ 4.73 (s, 5H, C_5H_5), 4.50 (s, 2H, C_5H_2), 2.79 (dt, 2H, $^2J_{HH}$ = 16.0 Hz, $^2J_{PH}$ = 2.8 Hz, CH_ACH_BP), 2.39 (dt, 2H, $^2J_{HH}$ = 16.0 Hz, $^2J_{PH}$ = 4.3 Hz, CH_ACH_BP), 1.25 (vt, 18H, J = 6.5 Hz, 2 ^{t}Bu), 1.13 (vt, 18H, J = 6.3 Hz, 2 ^{t}Bu), 0.55 (td, 3H, $^3J_{PH}$ = 3.4 Hz, $^3J_{HH}$ = 1.5 Hz, Ir-CH_3), −11.67 (tq, 1H, $^2J_{PH}$ = 14.8 Hz, $^3J_{HH}$ = 1.5 Hz, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 69.6.

Characterization of ***17****.* ^{1}H NMR (400.13 MHz, C_6D_6): δ 0.58 (td, 3H, $^3J_{PH}$ = 3.7 Hz, $^3J_{HH}$ = 1.5 Hz, Ir-CH_3), −10.83 (tq, 1H, $^2J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 1.5 Hz, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 64.5.

Reaction of 15 with a Large Excess of C_2H_5CHO with Formation of 18. The reaction was conducted in a manner similar to the aforementioned reaction of **6** with acetaldehyde. Starting from complex **3** (0.039 g, 0.050 mmol), ^{t}BuONa (0.015 g, 0.156 mmol), and C_2H_5CHO (2 mL, 28 mmol), complex **18** (0.033 g, 83%) was obtained as a yellow-orange powder. Anal. Calcd for $C_{31}H_{53}IrOP_2Ru$: C, 46.72; H, 6.70. Found: C, 46.80; H, 6.51. ^{1}H NMR (400.13 MHz, C_6D_6): δ 4.80 (s, 2H, C_5H_2), 4.62 (s, 5H, C_5H_5), 2.65 (dt, 2H, $^2J_{HH}$ = 16.6 Hz, $^2J_{PH}$ = 2.8 Hz,CH_ACH_BP), 2.39 (dt, 2H, $^2J_{HH}$ = 16.6 Hz, $^2J_{PH}$ = 4.6 Hz, CH_ACH_BP), 2.33 (q, 2H, $^3J_{HH}$ = 7.7 Hz, Ir-$COCH_2CH_3$), 1.36 (vt, 18H, J = 6.5 Hz, 2 ^{t}Bu), 1.23 (t, 3H, $^3J_{HH}$ = 7.7 Hz, Ir-$COCH_2CH_3$), 1.19 (vt, 18H, J = 6.3 Hz, 2 ^{t}Bu), −30.27 (t, 1H, $^2J_{PH}$ = 13.8 Hz, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 76.2. IR ($CHCl_3$, cm^{-1}): 1538 (s, Ir-$COCH_2CH_3$).

Synthesis of Complex 19. The reaction was conducted in a manner similar to the aforementioned synthesis of **10**. Starting from complex **18** (0.025 g, 0.031 mmol), **19** was obtained in almost quantitative yield as a yellow powder. Anal. Calcd for $C_{32}H_{53}IrO_2P_2Ru$: C, 46.59; H, 6.48. Found: C, 46.19; H, 6.83. ^{1}H NMR (400.13 MHz, C_6D_6): δ 4.56 (s, 5H, C_5H_5), 4.46 (s, 2H, C_5H_2), 2.61 (dt, 2H, $^2J_{HH}$ = 16.4 Hz, $^2J_{PH}$ = 2.8 Hz, CH_ACH_BP), 2.55 (q, 2H, $^3J_{HH}$ = 7.6 Hz, Ir-$COCH_2CH_3$), 2.30 (dt, 2H, $^2J_{HH}$ = 16.4 Hz, $^2J_{PH}$ = 4.5 Hz, CH_ACH_BP), 1.32 (t, 3H, $^3J_{HH}$ = 7.6 Hz, Ir-$COCH_2CH_3$), 1.16 (vt, 18H, J = 6.7 Hz, 2 ^{t}Bu), 1.19 (vt, 18H, J = 6.3 Hz, 2 ^{t}Bu), −8.39 (t, 1H, $^2J_{PH}$ = 14.8 Hz, Ir−H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 69.3 IR ($CHCl_3$, cm^{-1}): 2202 (w, Ir−H), 2012 (s, Ir-CO), 1597 (s, Ir-$COCH_3$).

Synthesis of Complex 19 with ^{13}C-Labeled CO. Complex **18** (0.0050 g, 0.006 mmol) was dissolved in C_6D_6 (0.6 mL) in a septum-capped NMR tube, and ^{13}CO (86.4 atom % ^{13}C) was slowly bubbled through the resulting solution via a needle for 30 min. A mixture of **19** and **19-^{13}CO** was formed in almost quantitative yield according to NMR. Selected signals for **19-^{13}CO** are as follows. ^{1}H NMR (400.13 MHz, C_6D_6): −8.39 (dt, 1H, $^2J_{CH}$ = 52.4 Hz, $^2J_{PH}$ = 14.7 Hz, Ir-H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 69.3. ^{13}C NMR (100.61 MHz, C_6D_6): δ 186.5 (dt, $^2J_{CH}$ = 52.4 Hz, $^2J_{CP}$ = 4.9 Hz, Ir-CO).

General Procedure for Transfer Dehydrogenation of ^{i}PrOH. The catalyst (typically near 0.030 mmol) and ^{t}BuONa (1.5 equiv) were placed into a Schlenk flask, and ^{i}PrOH (4000 equiv) and *tert*-butylethylene (4000 equiv) were added via syringe. The reaction mixture was stirred for 0.5 h, and aliquots were transferred to the Kontes flasks via cannula. The Kontes reactors were placed into the cavities of a heated aluminum block at specified temperatures. After the desired reaction time, the Kontes reactors were removed from the aluminum block and allowed to reach room temperature. The reaction mixtures were analyzed using ^{1}H NMR spectra.

General Procedure for Acceptorless Alcohol Dehydrogenation. The catalyst (typically near 0.015 mmol) and 1.5 equiv of ^{t}BuONa where necessary (for **1** and **3**) were placed into a Schlenk flask equipped with a magnetic stirring bar, and the desired alcohol (4000 equiv) was added via syringe. The Schlenk flask was equipped with a reflux condenser and placed into an oil bath heated at specified temperatures. A slow stream of Ar was passed above the reflux condenser to facilitate the escape of H_2. After the desired reaction time, the Schlenk flask was warmed to room temperature. The reaction mixtures were analyzed using ^{1}H NMR spectra. The side products 1,3-diphenyl-1-butanol,[49] 1,3-diphenyl-1-butanone,[50] (1-phenylethyl) ether,[51] and 2-cyclohexenyl-1-cyclohexanol[52] were identified by comparison of spectra with literature data. To our knowledge 3-cyclohexenyl-1-cyclohexanol was not reported previously. It was isolated by means of column chromatography on silica using hexane/CH_2Cl_2 1/1 as eluent in the form of a slightly yellowish oil; the sample contained a small amount of unidentified impurity which we were unable to separate; its signals are excluded from the spectrum. MS: m/z 91.1 (M + 2H). ^{1}H NMR (600.22 MHz, $CDCl_3$): δ 5.54−4.53 (m, 1H, −CH═C<), 3.36 (td, 1H, J_1 = 10.3 Hz, J_2 = 4.2 Hz, >C*H*(OH)−), 2.01−1.97 (m, 3H), 1.90−1.87 (m, 2H), 1.77−1.69 (m, 2H), 1.64−1.49 (m, 6H), 1.28−1.14 (m, 4H). ^{13}C{^{1}H} NMR (150.93 MHz, $CDCl_3$) 138.52, 124.49, 70.52, 55.09, 34.14, 30.03, 25.90, 25.31, 25.02, 24.98, 23.00, 22.73.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of compounds **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: koridze14@hotmail.com.

Notes

The authors declare no competing financial interest.

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