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Hydridoalkyl- and Hydridoalkenyliridium(III) Complexes Formed in the Reaction of (Carboranyl)iridium(III) Dihydrides with Alkenes and Alkynes. 1

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Reactions of isolated dihydridocarboranyliridium(III) complexes, $[Ir(H)_2(\sigma\text{-carb})(CO)(RCN)(PPh_3)]$ (carb = 7-C_6H_5-1,7-$C_2B_{10}H_{10}$; R = CH_3 (**2a**), C_6H_5 (**2b**)), with activated olefins and acetylenes such as $\overline{CH{=}CHC(O)OC(O)}$, $CH_2{=}CHCO_2R$ (R = CH_3, C_2H_5), *cis*- and *trans*-$CH(CO_2CH_3){=}CH(CO_2CH_3)$, $C(C_6H_5){\equiv}C(CO_2C_2H_5)$, and $C(CO_2CH_3){\equiv}C(CO_2CH_3)$ occur at room temperature to give hydridoalkyl- and hydridoalkenyliridium(III) derivatives, respectively, which are stable at room temperature and have been isolated as crystalline solids and fully characterized. The IR and ^1H NMR spectra of these organometallic products are discussed. In addition, the reductive elimination of the alkane or alkene molecule from the obtained hydrido complexes has also been investigated by ^1H NMR spectroscopy. Unsubstituted olefins such as 1-pentene or 1-hexene are instantaneously hydrogenated to the corresponding alkanes by reaction with the iridium(III) dihydrides, and no intermediate species could be detected by ^1H NMR spectroscopy. On the other hand, formation of thermally labile monohydrido alkenyl intermediates has been detected by monitoring with ^1H NMR spectroscopy the hydrogenation reactions of the acetylenes $CH_3C{\equiv}CH$, $CH_3C{\equiv}CCH_3$, $C_6H_5C{\equiv}CH$, and $C_6H_5C{\equiv}CC_6H_5$ with **2a** or **2b**. These iridium(III) monohydrido derivatives appear to be intermediate species in the homogeneous hydrogenation of alk-1-enes and alkynes catalyzed by the complexes $[Ir(\sigma\text{-carb})(CO)(RCN)(PPh_3)]$ (**1a** or **1b**).

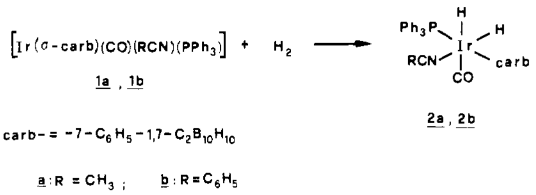
Introduction

The stoichiometric reactions of isolated dihydridometal complexes with unsaturated hydrocarbons have been scarcerly studied despite their pertinence to understanding of the stereochemistry and mechanism of the elemental steps involved in a catalytic hydrogenation reaction.[1-3] Thus, only a hydridoalkyl intermediate in the reaction of $(\eta^5\text{-}C_5H_5)_2WH_2$ with activated olefins[4] and a detailed study of the stoichiometric reactions between dihydridobis(η^5-cyclopentadienyl)molybdenum and activated olefins and acetylenes have been reported.[5] The latter reactions afforded hydridoalkyl and hydridoalkenyl complexes of general formula $(\eta^5\text{-}C_5H_5)_2MoHR$ which have been characterized and whose reductive-elimination reactions have also been investigated.[5] On the other hand, formation of thermally labile *cis*-hydridoalkyl- or alkenylmetal complexes has frequently been postulated as intermediate species in homogeneous catalytic hydrogenation of olefins and acetylenes.[6-8] However, the elusive nature of these organometallic intermediates generally has precluded their characterization, and thus the evidence supporting an intramolecular reductive-elimination of alkane or alkene from these intermediates as the final step in one catalytic hydrogenation system is indirect. Very recently, Halpern[9] was able to intercept a cationic hydridoalkylrhodium(III) intermediate formed in the course of the homogeneous hydrogenation of methyl (*Z*)-α-(acetamido)cinnamate catalyzed by the cationic complex 1,2-bis((diphenylphosphino)ethane)rhodium(I). The intermediate species was identified on the basis of its ^1H, ^{31}P, and ^{13}C NMR spectra at −78 °C in a deuteriomethanol solution.

We report here a study of the reactions of isolated *cis*-dihydridoiridium(III) complexes $[Ir(H)_2(\sigma\text{-carb})(CO)(RCN)(PPh_3)]$ (where carb = 7-C_6H_5-1,7-$C_2B_{10}H_{10}$; R = CH_3 (**2a**), C_6H_5 (**2b**)) with alkenes and alkynes.

Results and Discussion

Recently we have reported[10] the synthesis and chemistry of neutral carboranyliridium(I) complexes containing a nitrile ligand, $[Ir(\sigma\text{-car})(CO)(RCN)(PPh_3)]$ (carb = 7-C_6H_5-1,7-$C_2B_{10}H_{10}$; R = CH_3 (**1a**), C_6H_5 (**1b**)). These complexes, which are effective catalysts in the homogeneous hydrogenation of alk-1-enes and alkynes,[11] stereospecifically undergo oxidative addition of molecular hydrogen, yielding crystalline *cis*-dihydridoiridium(III) adducts, **2a** and **2b** (eq 1).[10] The isolated iridium(III) dihydrides **2a** and **2b** react with electrophilic alk-1-enes and alkynes in solution to give monohydridoalkyl- or alkenyliridium(III) derivatives, respectively. Their thermal stabilities are remarkable and, in agreement with the behavior generally found,[5] increase with increasing electron-withdrawing character of the substituents on the alkyl or alkenyl group. Thus, several hydridoalkyl- and hydridoalkenyliridium(III) complexes could be identified in solution by ^1H NMR spectroscopy or could be isolated as pure crystalline products and fully characterized (Table I and II).



(1)

(A) Reaction of 2a,b with Alkenes. Unsubstituted terminal olefins such as 1-pentene and 1-hexene instantaneously react with the iridium(III) dihydrides **2a** or **2b** in solution at room temperature yielding quantitatively the corresponding alkanes. The yellow color of the iridium(I) complex $[Ir(\sigma\text{-carb})(CO)(RCN)(PPh_3)]$ (**1a** or **1b**) appears immediately upon mixing the reactants, and no intermediate species could be observed by ^1H NMR spectroscopy at ambient temperature. On the other hand, activated olefin such as maleic anhydride, methyl or ethyl acrylate, dimethyl fumarate, or maleate react with the complexes **2a** or **2b** to give the corresponding monohydridoalkyl derivatives of iridium(III) which have been

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Table I. Analytical and IR Spectral Data

compd[a]	mp,[b] °C	anal. (calcd) % C	anal. (calcd) % H	anal. (calcd) % N	IR bands, cm^{-1} (Nujol)[c] ν(Ir–H)	ν(CO)	ν(C=O)	others
$Ir(H)_2(\sigma\text{-carb})(CO)(CH_3CN)L^d$ (**2a**)	84	46.92 (46.76)	4.60 (4.73)	1.76 (1.88)	2235 m, 2119 s	1992 vs		
$Ir(H)_2(\sigma\text{-carb})(CO)(C_6H_5CN)L^d$ (**2b**)	160	50.28 (50.60)	4.26 (4.62)	1.61 (1.73)	2114 s, 2110 s	1991 vs		2278 vw, ν(CN)
$Ir(H)[\sigma\text{-}CHCH_2C(O)OC(O)](\sigma\text{-carb})(CO)(CH_3CN)L$ (**3**)	137–138	46.97 (47.02)	4.25 (4.42)	1.57 (1.66)	2256 w	2043 vs	1825 vs	2321 w, ν(CN)
$Ir(H)[\sigma\text{-}CH_2CH_2C(O)OCH_3](\sigma\text{-carb})(CO)L$ (**4**)	142–143	46.85 (47.14)	4.76 (4.85)		2270 s	2006 vs	1630 vs	
$Ir(H)[\sigma\text{-}CH_2CH_2C(O)OC_2H_5](\sigma\text{-carb})(CO)L$ (**5**)	139–140	48.07 (47.81)	5.27 (5.02)		2270 m	2018 vs	1627 vs	
$Ir(H)[\sigma\text{-}CH(CO_2CH_3)CH_2C(O)OCH_3](\sigma\text{-carb})(CO)L$ (**6**)	159–160	46.48 (46.64)	4.94 (4.74)		2088 m	2022 vs	1690 vs, 1609 vs	
$Ir(H)[\sigma\text{-}C(C_6H_5){=}CHCO_2C_2H_5](\sigma\text{-carb})(CO)(C_6H_5CN)L$ (**7**)	136–137	56.03 (55.89)	5.03 (4.90)	1.36 (1.45)	2250 m	2039 vs	1688 m	1597 m, ν(C=C)[e]
$Ir(H)[\sigma\text{-}C(CO_2CH_3){=}CHCO_2CH_3](\sigma\text{-carb})(CO)(CH_3CN)L$ (**8a**)	154–155	48.03 (47.40)	4.43 (4.66)	1.43 (1.58)	2261 w	2046 vs	1711 vs	2321 vw, ν(CN), 1581 m, ν(C=C)
$Ir(H)[\sigma\text{-}C(CO_2CH_3){=}CHCO_2CH_3](\sigma\text{-carb})(CO)(C_6H_5CN)L$ (**8b**)	137–138	49.93 (50.62)	4.42 (4.57)	1.50 (1.48)	2258 w	2045 vs	1711 vs	2361 vw, ν(CN), 1581 m, ν(C=C)
$Ir(H)[\sigma\text{-}C{=}CHC(O)OC(O)](\sigma\text{-carb})(CO)(C_6H_5CN)L$ (**9**)	175–176	50.73 (50.55)	4.02 (4.13)	1.56 (1.55)	2270 w	2048 vs	1829 m, 1746 s	2322 w, ν(CN), 1540 m, ν(C=C)

[a] carb = $7\text{-}C_6H_5\text{-}1,7\text{-}C_2B_{10}H_{10}$; L = $P(C_6H_5)_3$. [b] All compounds melt with decomposition. [c] Key: s, strong; vs, very strong; m, medium; w, weak; vw, very weak; sh, shoulder. [d] Data from ref 10. [e] The ν(CN) band is probably masked by the ν(Ir–H) one.

isolated and characterized (complexes **3-6** of Table I and II). Thus, when a stoichiometric amount of maleic anhydride was added to a $CDCl_3$ solution of the complex **2a** at room temperature, a fast reaction (eq 2) occurred, giving the hydrido-

$$\underset{\mathbf{2a}}{[Ir(H)_2(\sigma\text{-carb})(CO)(CH_3CN)(PPh_3)]} + CH{=}CHC(O)OC(O) \rightarrow \underset{\mathbf{3}}{[Ir(H)[\sigma\text{-}CHCH_2C(O)OC(O)]\text{-}(\sigma\text{-carb})(CO)(CH_3CN)(PPh_3)]} \quad (2)$$

alkyliridium(III) derivative **3** which was isolated as white crystals. The ^1H NMR spectrum of the reaction mixture, run immediately after mixing the reagents, showed the replacement of the hydride resonance of **2a** (Table II) wiyh a new hydridic resonance at τ 28.0 (area 1, d, J_{PH} = 15.5 Hz) and a complex multiplet between τ 6.9 and 7.2 (area 3) due to the alkyl protons of $-CHCH_2C(O)OC(O)$ σ bonded to the metal. After the reaction mixture was allowed to stand for several hours at room temperature (or was rapidly warmed to 50 °C), these resonances were replaced by a singlet at τ 7.1 due to the succinic anhydride formed by reductive elimination from the complex **3** (eq 3). The IR spectrum (Nujol mull) of **3** ex-

$$\underset{\mathbf{3}}{[Ir(H)[\sigma\text{-}CHCH_2C(O)OC(O)]\text{-}(\sigma\text{-carb})(CO)(CH_3CN)(PPh_3)]} \rightarrow \underset{\mathbf{1a}}{[Ir(\sigma\text{-carb})(CO)(CH_3CN)(PPh_3)]} + CH_2CH_2C(O)OC(O) \quad (3)$$

hibited bands at 2321 w [ν(CN)], 2256 w [ν(Ir–H)], 2043 s [ν(CO)] cm^{-1} and very strong broad bands at 1825 and 1753 cm^{-1} attributed to ν(>CO) of the cyclic anhydride σ bonded to the iridium atom. Although the complete stereochemistry of the complex **3** has not been fully determined (15 geometric isomers can be drawn for this species), the obtained spectroscopic data were in agreement with a structure in which the hydride ligand is trans to the coordinated nitrile.[10]

Alkyl hydrides of iridium(III) stable toward the reductive-elimination reaction were obtained by reacting **2a** or **2b** with $CH_2{=}CH(CO_2R)$ (R = CH_3, C_2H_5) or with *cis*- and *trans*-$CH(CO_2CH_3){=}CH(CO_2CH_3)$. Thus, by reacting **2a** or **2b** with methyl and ethyl acrylate in CH_2Cl_2 solution at room temperature, the complexes $[Ir(H)[\sigma\text{-}CH_2CH_2C(O)OR](\sigma\text{-carb})(CO)(PPh_3)]$ (**4**, R = CH_3, and **5**, R = C_2H_5) were quantitatively obtained as white crystals. Their analytical and spectroscopic data were in accordance with the formation of six-coordinated hydridoalkyl derivatives in which the σ-bonded alkyl group acts a bidentate ligand through coordination of the ester carbonyl. In fact, the observed low value of the ester carbonyl stretching (1630 and 1627 cm^{-1} for **4** and **5**, respectively; Table I) in comparison with that shown by the uncomplexed ester (see below) was attributed to the decrease in the bond order of >C=O upon coordination to the metal atom.[12] Moreover, the high values of thee hydride chemical shift (doublet at ca. τ 33; Table II) and Ir–H stretching vibration (2270 cm^{-1}; Table I) observed for the complexes **4** and **5** suggested a configuration in which the hydride is trans to the coordinated ester carbonyl group of the alkyl ligand.[13] The complexes **4** and **5** appeared to be remarkably stable, and their benzene solution showed no decomposition upon heating at 60 °C for 30 min. However, when a CO stream was bubbled through a benzene solution of these complexes at room temperature, a fast displacement of the coordinated ester carbonyl group took place to yield dicarbonyl derivatives [Ir(H)(σ-

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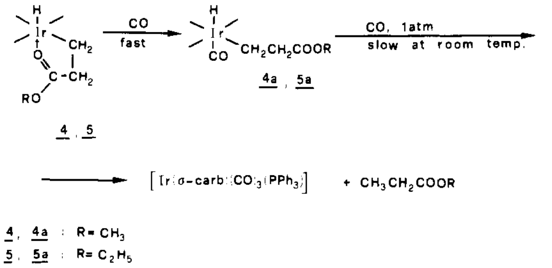
Table II. ^1H NMR Data[a,b]

compd	isomer	hydride resonances τ	mult[c]	J_{PH}, Hz	other proton resonances[d] τ
2a[e]		17.1	dd	20.1 (J_{HH} = 3.2)	
		28.2	dd	16.0 (J_{HH} = 3.2)	
2b[e]		17.0	dd	19.7 (J_{HH} = 2.7)	
		27.6	dd	15.5 (J_{HH} = 2.7)	
3		28.0	d	15.5	6.9-7.1 (3 H, m, >$CHCH_2$), 7.9 (3 H, s, CH_3CN)
4		33.2	d	16.5	7.6-8.9 (4 H, m, CH_2CH_2), 6.4 (3 H, s, OCH_3)
5		33.1	d	16.5	5.8-8.9 (9 H, m, CH_2CH_2 and OC_2H_5)
6	I	18.3	dd	16.5 (J_{HH} = 2.7)	6.7 (3 H, s, OCH_3), 6.9 (3 H, s, OCH_3)
	II	32.7	d	14.6	
	III	33.1	d	14.6	
7		27.6	d	11.4	3.7 (1 H, d, J_{PH} = 2.7, =CH)
8a	I	28.3	d	17.0	4.4 (1 H, d, J_{PH} = 2.3, =CH), 6.5 (3 H, s, OCH_3), 6.5 (3 H, s, OCH_3), 8.0 (3 H, s, CH_3CN)
	II	28.6	d	10.5	4.5 (1 H, d, J_{PH} = 2.3, =CH), 6.5 (3 H, s, OCH_3), 6.8 (3 H, s, OCH_3), 7.8 (3 H, s, CH_3CN)
8b	I	27.6	d	16.5	4.4 (1 H, d, J_{PH} = 2.3, =CH), 6.5 (3 H, s, OCH_3), 6.6 (3 H, s, OCH_3)
	II	27.7	d	10.1	4.3 (1 H, d, J_{PH} = 2.3, =CH), 6.4 (3 H, s, OCH_3), 6.8 (3 H, s, OCH_3)
9	I	27.3	d	7.8	3.8 (1 H, d, J_{PH} = 2.3, =CH)
	II	28.1	d	12.4	4.0 (1 H, d, J_{PH} = 2.3, =CH)

[a] Measured in $CDCl_3$ at ca. 27 °C and 60 MHz. [b] τ values ±0.05; J values ±0.1 Hz. Chemical shifts relative to Me_4Si (τ 10). [c] Key: s, singlet; d, doublet; dd, doublet of doublets; m, complex multiplet. [d] Parentheses indicate intensity, multiplicity, coupling constants, and assignment. [e] Data from ref 10.

$CH_2CH_2CO_2R)(\sigma\text{-carb})(CO)_2(PPh_3)]$ (**4a**, R = CH_3, **5a**, R = C_2H_5). These dicarbonyl species slowly underwent reductive elimination of propionic ester giving, under CO atomosphere, the iridium(I) complex $[Ir(\sigma\text{-carb})(CO)_3(PPh_3)]$, which has been previously described[10] (eq 4).



(4)

The IR spectrum of **4** in 1,2-dichloroethane showed bands at 2260 [ν(Ir—H)], 2010 [ν(CO)], and 1640 cm^{-1} [ν(>C=O)] of the ester carbonyl group coordinated to Ir] which, upon reaction with carbon monoxide at room temperature, were rapidly replaced by new bands at 2150 [ν(Ir—H)], 2075 and 2020 [ν(CO)], and 1725 cm^{-1} [ν(>C=O) of the uncoordinated corboxylate group]. This ligand displacement reaction was also followed by ^1H NMR spectroscopy. Thus, when carbon monoxide was bubbled through a $CDCl_3$ solution of **4** at room temperature, the hydride resonance at τ 33.2 rapidly disappeared, replaced by a new resonance at τ 18.9 (d, J_{PH} = 16.5 Hz) attributed to **4a** and typical of an hydride ligand trans to a CO group.[10] The latter resonance in turn disappeared in the course of ca. 4 h at 30 °C owing to reductive-elimination reaction of methyl propionate ($CH_3CH_2CO_2CH_3$) which was identified by its ^1H NMR spectrum.

Complexes **2a** and **2b** reacted with dimethyl maleate or fumarate in few minutes at room temperature to give the hydridoalkyl complex $\overline{Ir(H)[\sigma\text{-}CH(CO_2CH_3)CH_2C(O)}$-$OCH_3](\sigma\text{-carb})(CO)(PPh_3)]$ (**6**) as a mixture of three geometric isomers. Thus, when an excess of *cis-* or *trans-*$CH(CO_2CH_3)=CH(CO_2CH_3)$ was added to a $CDCl_3$ solution of complex **2a**, the ^1H(hydride) NMR spectrum of the reaction mixture showed the rapid appearance of a doublet of doublets at τ 18.3 (J_{PH} = 16.5 Hz; $^3J_{HH}$ = 2.7 Hz) and two doublets at τ 32.7 (J_{PH} = 14.6 Hz) and at τ 33.1 (J_{PH} = 14.6 Hz), respectively, of relative intensities 35:5:1. After the mixture was allowed to stand at room temperature, this intensity ratio changed and the equilibrium value 3.6:1:1 was attained in ca. 6 h. The high-field resonances at τ 32.7 and 33.1 were assigned to two isomeric species having both the hydrides trans to a coordinated ester carbonyl group,[13] as found for the complexes **4** and **5**. On the other hand, the low hydride chemical shift (τ 18.3) shown by the more abundant species was attributed to an hydrido complex isomer containing a strong trans-directing group trans to the hydride ligand. This is then consistent with a structure in which the hydride and CO ligands are mutually trans.[14] The splitting of the hydride resonance exhibited only by the latter isomer was attributed to coupling of the hydridic proton with the hydrogen on the α-carbon atom of the alkyl group σ bonded to the metal. This observed coupling may be originated by a particular geometry of this isomer of **6** in which the dihedral angle between the Ir-H and C-H bonds takes on a favorable value. In fact, it is well-known that a ^3J for coupling between protons on adjacent atoms is markedly affected by the geometry.[15] The IR spectrum (Nujol mull) of the isolated crystalline product **6** showed a medium band at 2088 cm^{-1} due to ν(Ir-H), a very strong carbonyl band at 2022 cm^{-1}, and two very strong bands at 1690 and 1609 cm^{-1} attributable to uncoordinated and coordinated ester carbonyl groups, respectively.

All of the three isomers of **6** were stable indefinitely toward the reductive-elimination reaction. Treatment of their solution with carbon monoxide (1 atm) at room temperature afforded the dicarbonylhydrido derivative $[Ir(H)[\sigma\text{-}CH(CO_2CH_3)\text{-}CH_2(CO_2CH_3)](\sigma\text{-carb})(CO)_2(PPh_3)]$ (**6a**) as unique isomer. Monitoring the carbonylation reaction of **6** in $CDCl_3$ by ^1H NMR spectroscopy, we have observed the progressive disappearance of the hydride signals at τ 18.3, 32.7, and 33.1 accompanied by the rising of a new doublet at τ 19.4 (J_{PH} = 17.4 Hz), indicative of the formation of a species having the hydride ligand trans to CO.[10] Further evidence that the carbonylation reaction of **6** occurred with displacement of the chelate ester carbonyl group was provided by IR spectroscopy. Thus, the

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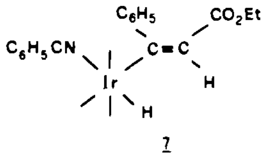
IR spectrum of **6** in CH_2Cl_2 solution showed two strong bands at 1685 and 1615 cm^{-1} assignable to the uncoordinated and coordinated ester carbonyl groups, respectively. These on treatment with carbon monoxide were gradually replaced by two strong bands at 1730 and 1705 cm^{-1} attributable to the stretching vibrations of two unequivalent noncoordinated ester carbonyl groups. Solutions of **6a**, unlike **4a** and **5a**, were stable at ambient temperature toward the reductive elimination of the saturated ester $CH_2(CO_2CH_3)CH_2(CO_2CH_3)$, but this reaction was found to occur quantitatively when a benzene solution of **6a** was heated at 60 °C for 3 h.

(B) Reaction of 2a,b with Alkynes. The reactions of the dihydrido complexes **2a** and **2b** with various alkynes have also been investigated. Bulkily substituted acetylenes do not react with **2a** and **2b**. Thus, when di-*ter*-butylacetylene was treated with **2a** or **2b** in benzene or chloroform solution at 40 °C for 12 h, the dihydride was quantitatively recovered. On the other hand, a fast reaction took place when a stoichiometric amount of **2a** or **2b** was treated with $CH_3C{\equiv}CH$, $t\text{-}C_4H_9C{\equiv}CH$, $C_6H_5C{\equiv}CH$, $CH_3C{\equiv}CCH_3$, or $C_6H_5C{\equiv}CC_6H_5$ in benzene or chloroform solution, yielding the iridium(I) complex **1a** or **1b**, respectively, and alkene as the hydrogenation product. By monitoring these reaction mixtures in $CDCl_3$ at low temperatures with ^1H NMR spectroscopy, it was possible to intercept thermally labile monohydridoalkenyliridium(III) derivatives formed as reaction intermediates through insertion of the acetylenic bond into one Ir–H bond of the dihydrides **2a** or **2b**. Thus, in the case of the reaction of **2b** with $C_6H_5C{\equiv}CH$, the ^1H NMR spectrum of the reaction mixture recorded at −10 °C showed fast replacement of the hydride resonance of **2b** (Table II) with a doublet at τ 27.4 (J_{PH} = 12.3 Hz). This resonance was assigned to a hydridic proton trans to the C_6H_5CN ligand of a hydridovinyl intermediate complex. The vinylic proton NMR pattern exhibited in the region between τ 4.1 and 4.5 was poorly resolved as the intermediate species underwent reductive elimination of styrene. Consequently, the stereochemistry around the double bond of the σ-bonded vinyl group could not be assigned. A more stable hydridovinyl intermediate was formed in the reaction between **2b** and diphenylacetylene in solution. In fact, monitoring this reaction mixture in $CDCl_3$ with ^1H NMR spectroscopy at room temperature, we observed the appearance of two doublets at τ 27.3 (J_{PH} = 16 Hz) and at τ 27.9 (J_{PH} = 12 Hz), in the intensity ratio 1:1. These resonances indicated the formation of two *cis*-hydridoalkenyliridium(III) isomers having both the hydride ligands in trans position to C_6H_5CN. The expected signals for the vinylic proton could not be detected, presumably being hidden beneath the phenyl proton pattern between τ 2.5 and 3.3. On standing at room temperature, both these hydridoalkenyl isomers underwent reductive-elimination reaction yielding stereospecifically and quantitatively *cis*-stilbene, as shown by the appearance in the proton NMR spectrum of the reaction mixture of a singlet at τ 3.6 due to the vinylic proton of this olefin.

Monohydridoalkenyliridium(III) complexes stable enough to be isolated as crystalline solids were obtained by reacting the dihydrido complexes **2a** or **2b** with alkynes activated by conjugation with electron-attracting groups such as CO_2R. Thus, the stoichiometric reaction between **2b** and $C_6H_5C{\equiv}CCO_2C_2H_5$ in benzene at room temperature afforded white crystals of $[Ir(H)[\sigma\text{-}C(C_6H_5){=}CH(CO_2C_2H_5)(\sigma\text{-carb})(CO)(C_6H_5CN)(PPh_3)]$ (**7**). Its IR spectrum (Table I) showed, in addition to the ν(Ir–H) and metal carbonyl bands, two medium absorptions at 1688 and 1597 cm^{-1} due to $\nu(>C{=}O)$ of the uncoordinated ester carbonyl group and to $\nu(>C{=}C<)$, respectively. The ^1H NMR spectrum ($CDCl_3$) of **7** (Table II) exhibited the hydride resonance as a doublet at τ 27.6 (J_{PH} = 11.4 Hz), indicating that the hydride proton is trans to the C_6H_5CN ligand and hence in cis position to the σ-bonded alkenyl group. In addition, the proton spectrum showed a doublet at τ 3.7 with J_{PH} = 2.7 Hz for the vinylic proton coupled to the ^{31}P nucleus of the phosphine ligand. The high vinylic proton shift observed is compatible with a proton in the geminal position to the COOR group.[12,16] Complex **7** in benzene solution underwent a reductive-elimination reaction upon heating to 50 °C, yielding stereospecifically *cis*-ethyl cinnamate (eq 5), detected by ^1H NMR spectroscopy.

$$\begin{aligned}&[Ir(H)[\sigma\text{-}C(C_6H_5){=}CH(CO_2C_2H_5)]\text{-}\\&\qquad\underset{\mathbf{7}}{(\sigma\text{-carb})(CO)(C_6H_5CN)(PPh_3)]}\rightarrow\\&\qquad\underset{\mathbf{1b}}{[Ir(\sigma\text{-carb})(CO)(C_6H_5CN)(PPh_3)]}+\\&\qquad\qquad cis\text{-}CH(C_6H_5){=}CHCO_2C_2H_5\quad(5)\end{aligned}$$

This reaction was completed in the course of few minutes. Thus, the data establish that complex **7** is a product of cis addition with the arrangement around the double bond of the σ-bonded vinyl group as shown



7

Dimethyl acetylenedicarboxylate reacted with **2a** and **2b** in benzene solution at room temperature to give the *cis*-hydridoalkenyliridium(III) adducts **8a** and **8b**, respectively, which could be isolated as white crystals stable indefinitely at ambient temperature. Both reaction products **8a** and **8b** turned out to be mixtures of two geometric isomers formed in the same ratio. In fact, the ^1H NMR spectra (Table II) of both these reaction products showed two sets of hydridic, vinylic, and methoxylic proton resonances in the relative intensity 1.5:1. The hydride resonances near τ 28, observed for all the adducts, are in agreement with structures in which the hydride and RCN ligands are mutually trans. The vinyl proton resonance appeared as doublets in the range τ 4.3–4.5 owing to the coupling with ^{31}P nucleus of the phosphine ligand (J_{PH} = 2.3 Hz). Furthermore, each isomer showed two singlets between τ 6.4 and 6.8 due to the protons of two nonequivalent OCH_3 groups.

When toluene solutions of either **8a** and **8b** (mixtures of the two isomers) were heated at temperatures up to 80 °C, a slow reductive-elimination reaction took place and the colorless initial solutions turned to yellow owing to formation of the iridium(I) complex **1a** or **1b**. The GLC product analyses showed the formation of dimethyl maleate together with small amount of dimethyl fumarate. The ratio fumarate/maleate was found to increase on increasing the reaction time as a consequence of cis → trans isomerization catalyzed by the iridium(I) complex produced in the course of the elimination reaction. In fact, this was proved on heating at 80 °C a toluene mixture containing an authentic sample of dimethyl maleate and catalytic amount of the iridium(I) complex **1a**.[17] Thus, the evidence confirmed that the insertion reaction of acetylendicarboxylate into one Ir–H bond of the dihydrides **2a** or **2b** is stereospecifically cis, yielding the adducts **8a** and **8b**, respectively.

Further evidence of a cis arrangement around the double bond for the complex **8b** was obtained by treating a benzene solution of this complex (mixture of the isomers I and II of Table II) with anhydrous HCl at room temperature. The slow intramolecular condensation reaction (eq 6) occurred quan-

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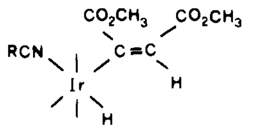
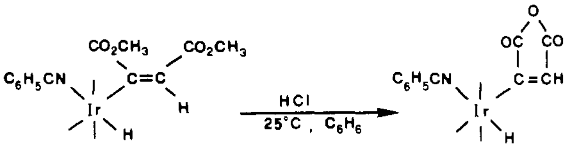
(16) C. S. Kraihanzel and L. G. Herman, *J. Organomet. Chem.*, **15**, 397 (1968).

(17) S. Bresadola and B. Longato, to be submitted for publication.



8

a, R = CH_3; b, R = C_6H_5



(6)

8b 9

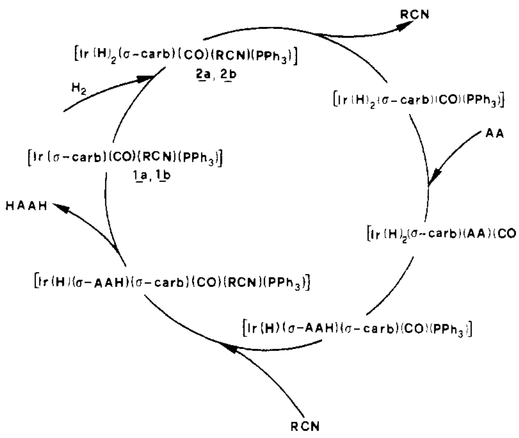
titatively in the course of several hours. The reaction product **9** was isolated as white crystals. Its IR spectrum (Nujol mull) exhibited (Table I), in addition to the ν(Ir–H) and metal carbonyl absorptions, two bands at 1829 and 1746 cm^{-1} due to the symmetric and antisymmetric stretching vibrations, respectively, of the carbonyl group of the cyclic anhydride[18,19] σ bonded to the metal. The ^1H NMR spectrum of **9** in $CDCl_3$ showed (Table II) the hydride resonance as two doublets at τ 27.3 and 28.1 of relative intensity 1.25:1 in agreement with the formation of two isomeric adducts both with the hydride and C_6H_5CN ligands mutually trans. The proton spectrum also revealed two doublets at τ 3.8 and 4.0 (intensity ratio of 1.25:1) attributable to the vinylic proton, coupled with ^{31}P nucleus of the phosphine ligand (J_{PH} = 2.3 Hz), of the two geometric isomers.

Upon heating of the $CDCl_3$ solution of **9** to 50 °C for several minutes, reductive elimination of maleic anhydride occurred as shown by the ^1H NMR and IR spectra of the resulting mixture.

Conclusion

The *cis*-dihydrido complexes **2a** and **2b** readily react with terminal olefins and acetylenes forming monohydridoalkyl- or monohydridoalkenyliridium(III) derivatives through monoinsertion into one of the Ir–H bonds. Diisertion reactions have never been observed even in the presence of a large excess of the unsaturated substrate. The reluctance of the monohydrido species to react with a second molecule of alkene or alkyne is likely attributable to crowding effects of the ligands coordinated to the metal. In fact, the steric requirements of the bulky carboranyl and triphenylphosphine ligands should prevent the accommodation of a second alkyl or alkenyl group around the metal atom. Likewise, steric effects are also responsible for the observed inertness of both the complexes **2a** and **2b** toward internal olefins and hindered acetylenes such as cyclohexene and di-*tert*-butylacetylene. The observed thermal stabilities for the monohydridoalkyl- and monohydridoalkenyliridium(III) complexes here described are remarkable and increase with increasing electron-withdrawing properties of the substituents on the alkyl or alkenyl group, in agreement with a trend previously noted for metal–carbon σ–bond stabilities.[20] The enhanced stabilities of our complexes compared to those generally observed for hydridoalkyl and -alkenyl derivatives of transition metals may be explained in terms of both steric and electronic effects arising from the bulky electron-withdrawing carboranyl group coordinated to the metal atom. On the basis of the results thus far obtained, these factors cannot be separately evaluated, but we suggest that steric effects play an important role in increasing the kinetic stability of the hydridocarboranyl complexes toward reductive elimination of the alkane or alkene. These organometallic adducts, with the exception of those formed by reaction of **2a** or **2b** with olefins activated with carboxylate groups, in turn undergo thermal reductive elimination yielding the corresponding hydrogenated hydrocarbon and the iridium(I) complex **1a** or **1b**. As the latter iridium(I) derivatives easily add molecular hydrogen to reform the dihydrides **2a** and **2b**,[10] in principle the stoichiometric reactions reported here can be made catalytic under a hydrogen atmosphere at an appropriate temperature.[17] In fact, it was observed that the hydrogenation of maleic anhydride to succinic anhydride catalyzed by the dihydride **2a** or **2b** occurs under hydrogen at an appreciable rate above 40 °C. At lower temperatures, the initially formed hydridoalkyl complex **3** is stable toward reductive elimination of succinic anhydride. Thus, the hydridoalkyl- and hydridoalkenyliridium(III) complexes formed in the reaction of **2a** or **2b** with olefins or acetylenes are really reaction intermediates of the overall catalytic hydrogenation cycle, which then appears to take place through a "hydride route",[2] as depicted in Scheme I.

Scheme I



AA = $>C=C<$, $-C\equiv C-$

carb = $-7-C_6H_5-1,7-C_2B_{10}H_{10}$

R = CH_3, C_6H_5

The observed stabilities of the monohydrido intermediates strongly suggest that the alkane or alkene reductive-elimination process constitutes the rate-determining step of the catalytic cycle. Catalytic hydrogenation of olefins having carboxylate substituents on the unsaturated carbon atoms is prevented by the formation of thermally stable chelate hydridoalkyl complexes such as the derivatives **4–6** (Tables I and II). On treatment of these chelate complexes with carbon monoxide, displacement of the coordinated ester carbonyl occurs with formation of dicarbonyl derivatives which then undergo alkane reductive elimination, yielding a dicarbonyliridium(I) complex. The complex so formed adds molecular hydrogen giving the dihydrido complex $[Ir(H)_2(\sigma\text{-carb})(CO)_2(PPh_3)]$,[10] which is unreactive toward unsaturated hydrocarbons. This lack of reactivity is understandable when one considers that this dihydridodicarbonyl complex, unlike the dihydrides **2a** and **2b** containing the "labile" nitrile ligand, shows no measurable ligand dissociation in solution.

Kinetic measurements for the overall catalyzed hydrogenation reaction as well the reductive elimination step are currently in progress.

Experimental Section

Reagent grade solvents were further purified by standard methods and were dried and degassed before use. The dihydrides $[Ir(H)_2$-

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(σ-carb)(CO)(RCN)(PPh$_3$)] (**2a**, R = CH$_3$, and **2b**, R = C$_6$H$_5$) were prepared as previously reported.[10] The reactant alkenes and alkynes were commercial samples used without further purification. Infrared spectra were obtained with a Perkin-Elmer Model 457 and calibrated against polystyrene film. ^{1}H NMR spectra were recorded on a Bruker WP-60 FT NMR instrument at 60 MHz in CDCl$_3$ or C$_6$D$_6$ solutions. Melting points were determined by a conventional hot-stage microscope and are uncorrected. Molecular weights were obtained by a Mechrolab Model 301A osmometer.

[Ir(H)[σ-CHCH$_2$C(O)OC(O)](σ-carb)(CO)(CH$_3$CN)(PPh$_3$)] (3). An excess of maleic anhydride (144 mg, 1.5 mmol) was added to a solution of complex **2a** (380 mg, 0.51 mmol) in benzene (5 mL) at room temperature under argon atmosphere. After a few minutes, addition of hexane (10 mL) afforded a white solid. This crude product was separated and further purified by recrystallization from hexane/benzene (1:1) to give 340 mg (yield 80%) of pure **3**.

Ir(H)[σ-CH$_2$CH$_2$C(O)OCH$_3$](σ-carb)(CO)(PPh$_3$) (4). Methyl acrylate (0.2 mL, 0.2 mmol) was added to a dichloromethane solution of **2b** (162 mg, 0.2 mmol; in 2 mL of CH$_2$Cl$_2$) at room temperature under argon. After 1 h of stirring, removal of the solvent under vacuum and recrystallization of the residual solid from CH$_2$Cl$_2$/CH$_3$OH gave white crystals of pure **4** (142 mg, 90%): mol wt (CHCl$_3$) found 820, calcd 790.

Ir(H)[σ-CH$_2$CH$_2$C(O)OC$_2$H$_5$](σ-carb)(CO)(PPh$_3$) (5). Complex **5** was prepared as **4** by reacting the dihydride **2a** with ethyl acrylate in dichloromethane. The yield of white crystals of **5** was 85%.

Ir(H)[σ-CH(CO$_2$CH$_3$)CH$_2$C(O)OCH$_3$](σ-carb)(CO)(PPh$_3$) (6). Methyl fumarate (200 mg, 1.39 mmol) was reacted with complex **2b** (405 mg, 0.50 mmol) in CH$_2$Cl$_2$ (5 mL) solution under argon. The resulting mixture was stirred at room temperature for 5 min. Then, methanol (10 mL) was added, and the precipitate so formed was separated by filtration and further purified by recrystallyzation from CH$_2$Cl$_2$/CH$_3$OH (1:1). Pure white crystals of **6** were obtained in a yield of 80% (337 mg). Following the same procedure, complex **6** was obtained by reacting the complex **2a** or **2b** with methyl maleate in place of methyl fumarate.

Ir(H)[σ-C(C$_6$H$_5$)=CH(CO$_2$C$_2$H$_5$)](σ-carb)(CO)(C$_6$H$_5$CN)(PPh$_3$) (7). A solution of 403 mg (0.5 mmol) of complex **2b** in 5 mL of benzene was treated with an excess of C$_6$H$_5$C$\equiv$CCO$_2$C$_2$H$_5$ (122 mg, 0.7 mmol) at room temperature. After 10 min of stirring, the solvent was removed under reduced pressure to give a white solid; this was then crystallized from hexane/benzene (1:1) to give 417 mg (85 %) of white crystals of pure **7**.

Ir(H)[σ-C(CO$_2$CH$_3$)=CH(CO$_2$CH$_3$)](σ-carb)(CO)(CH$_3$CN)(PPh$_3$) (8a). A solution of the dihydride **2a** (745 mg, 1 mmol) and dimethyl acetylendicarboxylate (0.5 mL, 5 mmol) in benzene (10 mL) was stirred for a few minutes at room temperature under argon. Then, upon addition of hexane (20 mL), a precipitate was formed which was further purified by recrystallization from hexane/benzene (1:1) to give 816 mg (92 %) of white crystals of **8a**: mol wt (CHCl$_3$) found 880, calcd 886.9.

Ir(H)[σ-C(CO$_2$CH$_3$)=CH(CO$_2$CH$_3$)](σ-carb)(CO)(C$_6$H$_5$CN)(PPh$_3$) (8b). As with the complex **8a**, this was prepared by treating 805 mg (1 mmol) of the dihydride **2b** with 5 mmol (0.5 mL) of C(CO$_2$CH$_3$)$\equiv$C(CO$_2$CH$_3$) in benzene (10 mL). Addition of hexane caused precipitation of **8b** that was then purified by recrystallization from hexane/benzene to give 900 mg (95 %) of white crystals of pure product: mol wt (CHCl$_3$) found 920, calcd 949.

Ir(H)[σ-C=CHC(O)OC(O)](σ-carb)(CO)(C$_6$H$_5$CN)(PPh$_3$) (9). A slow stream of anhydrous hydrogen chloride was passed into a benzene solution of **8b** (300 mg in 8 mL) for 10 h at room temperature. The white solid so formed was purified by recrystallization from hexane/benzene to give white crystals of pure **9** in essentially quantitative yield: mol wt (CHCl$_3$) found 890, calcd 903.

Acknowledgment. We thank the Italian Research Council, CNR, for a grant in support of this research.

Registry No. **2a**, 70700-92-4; **2b**, 70700-93-5; **3**, 79255-31-5; **4**, 79255-30-4; **5**, 79255-29-1; **6**, 79255-28-0; **7**, 79255-27-9; **8a**, 79255-26-8; **8b**, 79255-25-7; **9**, 79272-63-2.

Contribution from the Departments of Chemistry,
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Ligand Substitution Properties of the MFe$_3$S$_4$ Double-Cubane Cluster Complexes [Mo$_2$Fe$_6$S$_8$(SR)$_9$]$^{3-}$ and [M$_2$Fe$_7$S$_8$(SR)$_{12}$]$^{3-}$ (M = Mo, W)

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Reactions of the double-cubane clusters [Mo$_2$Fe$_6$S$_8$(SEt)$_9$]$^{3-}$ (**1**) and [M$_2$Fe$_7$S$_8$(SEt)$_{12}$]$^{3-}$ (**3**, M = Mo, W) with benzenethiol and acetyl chloride have been investigated in order to ascertain ligand substitution propensities of thiolate ligands. These complexes contain individual MoFe$_3$S$_4$(SEt)$_3$ clusters connected by (μ-SEt)$_3$ or (μ-SEt)$_3$Fe^{III}(μ-SEt)$_3$ bridging groups and thus offer as potential reaction sites both terminal and bridging thiolate sulfur atoms. Reactions of **1** with 1–6 and larger equiv of reagent were monitored by UV–visible spectrophotometry, ^{1}H NMR spectroscopy, and differential-pulse polarography. The limiting substituted species formed were [Mo$_2$Fe$_6$S$_8$(μ-SEt)$_3$(SPh)$_6$]$^{3-}$ (**5**) and [Mo$_2$Fe$_6$S$_8$(μ-SEt)$_3$Cl$_6$]$^{3-}$ (**4**), salts of which were isolated in good yield when reactions with $\gtrsim$6 equiv of reagent were conducted on a preparative scale. Preparative reactions of **3** and $\gtrsim$6 equiv of reagent afforded isolated salts of [Mo$_2$Fe$_7$S$_8$(μ_2-SEt)$_6$(SPh)$_6$]$^{3-}$ (**8**) and [M$_2$Fe$_7$S$_8$(μ-SEt)$_6$Cl$_6$]$^{3-}$ (**7**). Similarly, [W$_2$Fe$_6$S$_9$(SEt)$_8$]$^{3-}$ (**2**) yielded [W$_2$Fe$_6$S$_8$(μ-S)(μ-SEt)$_2$(S-*p*-tol)$_6$]$^{3-}$ (**6**) with *p*-toluenethiol. Structures of all products are fully documented by spectroscopic and electrochemical properties. These results lead to the conclusion that the two electrophilic reagents effect only terminal ligand substitution under reaction conditions (Me$_2$SO or acetonitrile solutions, ambient temperature, stoichiometric or (specified) excess of reagent) that leave intact individual cluster structures. A reported exception to this consistent reactivity pattern, viz., formation of [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ from the reaction of **1** with excess 2-hydroxyethanethiol, was not confirmed. By comparison of properties of authentic [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$, prepared by direct synthesis, the ligand exchange product isolated in this work was shown to be [Mo$_2$Fe$_6$S$_8$(μ-SEt)$_3$(SCH$_2$CH$_2$OH)$_6$]$^{3-}$. The bridge structure of the precursor cluster is retained, as in the formation of **4–8** by similar reactions.

Introduction

Three structural types of double-cubane cluster complexes containing MFe$_3$S$_4$ core units, [Mo$_2$Fe$_6$S$_8$(SR)$_9$]$^{3-}$[2] (**1**), [M$_2$Fe$_6$S$_9$(SR)$_8$]$^{3-}$[2,3] (**2**), and [M$_2$Fe$_7$S$_8$(SR)$_{12}$]$^{3-}$[3] (**3**) (M = Mo, W), shown in Figure 1, have been prepared and characterized in these laboratories. Structures of the Mo clusters **1–3** have been established by X-ray crystallography.[2,4] In

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