suggests significant π bonding to this moiety as well,[21] which would alter the hybridization state of the bonded oxygen. This bond is substantially shorter than the 2.28-Å distance to the water molecule in *trans*-$[O(OH_2)((acac)_2en)Tc]^+$ and the more typical 2.02-Å Tc(V)–O single-bond distances evident in the equatorial oxygens in this structure.[20] While the abnormally large Tc–O1–C11 bond angle of 154° must largely result from steric repulsion between the methylene hydrogens of the ethoxo group and the adjacent Br1, expansion of this angle should also be facilitated by a change in hybridization on the oxygen from approximately sp^3 in free ethanol to substantially sp^2, when involved in π bonding to the echnetium.

The downfield ^1H NMR shifts of the ring protons, which is attenuated by distance, and the upfield shifts of the alkoxo protons, which is larger for the methyl protons on the ethoxo relative to the methoxo ligands, are understandable on the basis of an anisotropic magnetic field generated by the circulation of electrons around the Tc=O bond. Reference to Figure 1 shows that the appreciable upfield shift for the methyl protons on the ethoxo ligands results from their being closer to the dipolar (Tc=O) axis than the methylene protons.[24]

While the electronic, infrared, and NMR spectra of these complexes are similar to their cis analogues with bipyridine ligands, steric requirements imposed by the bulky halide ions generally cause the pyridines to adopt a trans arrangement in similar transition-metal complexes.[8] In doing so the pyridines are allowed some degree of rotational flexibility around their Tc–N bonds, and packing forces result in their being canted at 30 and 40° from the plane of the two oxygens and two nitrogens. The twisting of the nitro groups out of planarity with the pyridine rings is not particularly unusual. While this group is strictly coplanar with the aromatic ring in crystalline nitrobenzene,[25] in other aromatic rings containing the nitro substituent steric factors twist this group out of planarity. For example, the dihedral angle between between the aromatic ring and the nitro group is 3.0° in *p*-nitrotoluene[26] and 9.5° in *p*-dinitrobenzene.[27] Steric factors also cause the nitro group to be twisted by 64° in 9,10-dinitroanthracene and even to 85° in 9-nitroanthracene.[25] The steric interaction between the nitro groups on translationally related molecules in the unit cell appears to cause the distinct twists out of planarity with the pyridine rings in the structure of $[O(CH_3CH_2O)Br_2(Npy)_2Tc^V]$.

Acknowledgment. This work was supported by PHS Grants CA24344 and GM26390. The able assistance of John Child of the Boston College Computer Center in configuring the X-ray programs for the IBM-VMS operating system is also appreciatively recognized.

Registry No. $[O(MeO)Cl_2(Cpy)_2Tc]$, 92622-14-5; $[O(EtO)Cl_2(Cpy)_2Tc]$, 92622-15-6; $[O(MeO)Br_2(Cpy)_2Tc]$, 92622-16-7; $[O(EtO)Br_2(Cpy)_2Tc]$, 92622-17-8; $[O(EtO)Cl_2(Npy)_2Tc]$, 92622-18-9; $[O(EtO)Br_2(Npy)_2Tc]$, 92622-19-0; $[O(EtO)Cl_2(bpy)Tc]$, 92622-20-3; $[O(EtO)Cl_2(Me_2bpy)Tc]$, 92622-21-4; $[n\text{-}Bu_4N][^{99}TcOBr_4]$, 92622-23-6; $[n\text{-}Bu_4N][^{99}TcOCl_4]$, 92622-25-8.

Supplementary Material Available: Listings of hydrogen atom positions (Table Is), temperature factors for non-hydrogen atoms (Table IIs), bond distances and angles for complete structures (Tables IIIs and IVs), calculated and observed structure factor amplitudes for $[O(CH_3CH_2O)Br_2(Npy)_2Tc^V]$ (Table Vs), and electronic spectra for $[O(RO)X_2L_2Tc^V]$ (Table VIs) (14 pages). Ordering information given on any current masthead page.

(21) From a modification of Pauling's bond order relation[22] with standard average Tc–O bond lengths[3,13,23] taken to be Tc–O = 1.98 Å, Tc=O = 1.74 Å, and Tc≡O = 1.65 Å yields a Tc–O bond order of 2.54 and a Tc–OR bond order of 1.45.

(22) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 239.
(23) Kastner, M. E.; Fackler, P. H.; Clarke, M. J. *Inorg. Chim. Acta*, in press.

(24) The methylene protons are an average of 1.5 Å from the Tc=O axis, while those on the second carbon spend a significant amount of time as close as 0.5 Å from this axis with the average distance being 1.0 Å.

(25) Trotter, J. *Acta Crystallogr.* **1959**, *12*, 887–888.
(26) Barve, J. F.; Pant, L. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *B27*, 1158–1162.
(27) Abrahams, S. C. *Acta Crystallogr.* **1950**, *3*, 194–196.

Contribution from the Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione del CNR, Istituto di Chimica Analitica dell'Università di Padova, Padova, Italy, and Istituto di Chimica dell'Università di Trieste, Trieste, Italy

Kinetic and Mechanistic Study of the Succinic Anhydride Reductive-Elimination Reaction from the Six-Coordinate $Ir(H)[\sigma\text{-}\overline{CHCH_2C(O)OC(O)}](\sigma\text{-carb})(CO)(PhCN)(PPh_3)$ Complex

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The hydridoalkyliridium(III) complex $Ir(H)[\sigma\text{-}\overline{CHCH_2C(O)OC(O)}](\sigma\text{-carb})(CO)(PhCN)(PPh_3)$, where carb = 7-$C_6H_5$-1,7-$C_2B_{10}H_{10}$, undergoes reductive-elimination reaction of succinic anhydride under mild conditions. This reaction, which represents a crucial step in the homogeneous hydrogenation of maleic anhydride catalyzed by the four-coordinate iridium(I) complex $Ir(\sigma\text{-carb})(CO)(PhCN)(PPh_3)$ at T = 50 °C (P_{H_2} = 1 atm), has been kinetically investigated in 1,2-dichloroethane solution by IR spectroscopy between 35 and 45 °C. The elimination reaction implies preliminary PhCN dissociation to give a five-coordinate intermediate that then undergoes intramolecular reductive elimination of succinic anhydride. The obtained activation parameters indicate that the reductive elimination of succinic anhydride from the five-coordinate hydridoalkyliridium(III) intermediate is a highly concerted process whose drawing force is the incipient formation of the strong C–H bond of the product.

Introduction

We have previously reported that iridium(I) complexes of the type $Ir(\sigma\text{-carb})(CO)(RCN)(PPh_3)$, where carb = 7-$C_6H_5$-1,7-$C_2B_{10}H_{10}$ and R = CH_3 or C_6H_5, are efficient hydrogenation catalysts for a series of terminal alkenes and of alkynes.[1] The hydrogenation reaction occurs at room temperature with unactivated olefins, whereas higher temperatures

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(1) Morandini, F.; Longato, B.; Bresadola, S. *J. Organomet. Chem.* **1982**, *239*, 377.

 Inorganic Chemistry, Vol. 23, No. 24, 1984

(>50 °C) are required with alkenes or alkynes bearing electron-withdrawing substituents. In fact, in the latter cases, the catalytic hydrogenation at room temperature is prevented by the formation of hydrido alkyl or hydrido alkenyl intermediates thermally stable toward the reductive elimination.

Thus, a number of these complexes of general formula Ir(H)R′(σ-carb)(CO)(RCN)(PPh_3) (R′ = $CHCH_2C(O)OC(O)$, R = CH_3; R′ = $C(C_6H_5) = CH(CO_2C_2H_5)$, R = C_6H_5; R′ = $C(CO_2CH_3) = CH(CO_2CH_3)$, R = CH_3 or C_6H_5) have been isolated from the reaction of the dihydrides Ir(H_2)(σ-carb)(CO)(RCN)(PPh_3) with the appropriate alkene or alkyne.[2] When they are heated in solution of benzene or 1,2-dichloroethane, these complexes undergo reductive elimination of the substituted alkyl or alkenyl ligand, restoring the catalyst iridium(I) complex Ir(σ-carb)(CO)(RCN)(PPh_3).

The remarkable stability of these hydrido alkyl and hydrido alkenyl derivatives offers the unique opportunity of studying kinetically the reductive-elimination reaction that appears to be the product-forming step in these homogeneous catalytic hydrogenations. Moreover, the formation of hydrido alkyl and hydrido alkenyl complexes (as intermediate species) is generally thought a key step in the catalytic hydrogenation of unsaturated substrates, but only in a very few cases such intermediates have been detected or isolated. The first one is represented by the cationic complex $[Rh(H)[C(CH_2Ph)(CO_2CH_3)(NHC(O)CH_3)](dpe)S]^+$, stable only at temperature <−40 °C.[3] In addition, the more stable complexes *cis*-$Rh(H)(CH_2COR)(PMe_3)_2Cl$ (R = CH_3, C_6H_5) have been recently isolated, and a kinetic study of acetone reductive elimination has been reported.[4]

In this paper we describe the kinetics and the mechanism of the reductive-elimination reaction of succinic anhydride from the complexes Ir(H)[σ-$CHCH_2C(O)OC(O)$](σ-carb)(PhCN)(CO)PPh_3 carried out in 1,2-dichloroethane solution between 35 and 45 °C by IR monitoring of the reaction mixtures in the range 2300–1700 cm^{-1}.

This investigation follows our recent study on the carborane reductive elimination from the hydrido(carboranyl)iridium(III) complex, Ir(H)(Cl)(σ-carb)(CO)$(PPh_3)_2$.[5]

Experimental Section

Materials. The complex Ir(H)[σ-$CHCH_2C(O)OC(O)$](σ-carb)(CO)(PhCN)(PPh_3) (**1**) was prepared by stirring a suspension of Ir(σ-carb)(CO)(PhCN)(PPh_3) (**2**) (400 mg, 0.5 mmol) in 1,2-dichloroethane (5 mL) under hydrogen (1 atm) for ca. 30 min at room temperature. The pale yellow solution so formed was added to a solution of $CH{=}CHC(O)OC(O)$ (117 mg, 1.2 mmol) in 1,2-dichloroethane (2 mL), and the reaction mixture was then stirred under nitrogen atmosphere for a few minutes at room temperature. Addition of *n*-hexane (40 mL) afforded a white solid that was separated by filtration. Recrystallization of the crude product under N_2 from 1,2-dichloroethane/*n*-hexane gave white microcrystals of **1**, yield 310 mg (70%). Anal. Calcd. for $C_{38}H_{39}B_{10}NO_4PIr$: C, 50.43; H, 4.34; N, 1.55. Found: C, 49.81; H, 4.35; N, 1.81. ^{1}H NMR (C_6D_6): τ 27.6 [d, *J*(P–H) = 16 Hz, IrH], 6.6–7.3 [complex m, −$CHCH_2C(O)OC(O)$], 2.4–3.3 [complex pattern, $P(C_6H_5)_3$, C_6H_5CN, and C_6H_5 of the carboranyl group]. IR (Nujol): 2290 (w, ν(CN)), 2240 (m, ν(IrH)), 2046 and 2031 (vs, ν(CO)), 1823 and 1754 cm^{-1} (s, br, ν(>CO)).

The complex Ir(H)[σ-$CHCH_2C(O)OC(O)$](σ-carb)$(CO)_2$(PPh_3) (**3**) was prepared by stirring a solution of complex **1** (100 mg, 0.11 mmol) in 1,2-dichloroethane (2.5 mL) under CO (1 atm) for a few minutes at room temperature. A 40-mL portion of *n*-hexane was then added, and the resulting solution was stored at 0 °C. A white crystalline precipitate of **3** was slowly formed that was separated by filtration, washed with *n*-hexane, and dried: yield 50 mg (60%); mp 140–142 °C dec. Anal. Calcd for $C_{32}H_{34}B_{10}O_5PIr$: C, 46.31; H, 4.13. Found: C, 46.07; H, 4.61. IR (Nujol): 2175 (s, ν(Ir–H)), 2089 (vs), 2050 (vs, ν(CO)), 1845 (s), 1830 (s), 1760 cm^{-1} (br, s, ν(>CO)). ^{1}H NMR ($CDCl_3$): τ 19.5 [d, *J*(P–H) = 15.5 Hz, Ir–H], 6.7–7.9 [complex m, −$CHCH_2C(O)OC(O)$], 2.5–2.8 [complex pattern, C_6H_5 protons of the phosphine and carboranyl ligands]. The hydride resonance at τ 19.5 indicates that the hydride ligand is trans to a CO group, as previously found for related complexes.[2]

Triphenylphosphine and benzonitrile (EGA products) were purified by recrystallization from CH_2Cl_2/CH_3OH and distillation, respectively. The reagent grade solvents were purified by standard methods and degassed before use.

Argon and carbon monoxide were high-purity SIO products. Infrared spectra were obtained with a Perkin-Elmer Model 457 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker WP-60 FT NMR instrument at 60 MHz.

Procedure. The reductive-elimination reaction of succinic anhydride was investigated by IR monitoring 1,2-dichloroethane solutions prepared by transferring under Ar (or under CO) carefully deoxygenated phosphine and nitrile solutions or the pure solvent into a Schlenk tube containing a weighted quantity of **1**. The reactions were followed by sampling, through a stainless-steel capillary system, aliquot portions of the reacting solutions. Samples were ejected directly into IR cells and spectra recorded immediately in the CO stretching region, reference cells being filled with matching PPh_3 or PhCN when appropriate.

Reductive-Elimination Reaction. Dichloroethane solutions of complex **1** under argon give, quantitatively, succinic anhydride and the iridium(I) complex Ir(σ-carb)(CO)(PhCN)(PPh_3) (**2**) according to eq 1.

$$\underset{\mathbf{1}}{Ir(H)[\sigma\text{-}CHCH_2C(O)OC(O)](\sigma\text{-carb})(CO)(PhCN)(PPh_3)} \xrightarrow{DCE} \underset{\mathbf{2}}{Ir(\sigma\text{-carb})(CO)(PhCN)(PPh_3)} + CH_2CH_2C(O)OC(O) \quad (1)$$

Analyses of the changes of the absorbance in the range 2300–1700 cm^{-1} show the decrease of the absorptions at 2045 and 1760 cm^{-1} attributed to the therminal CO and coordinated anhydride carbonyls, respectively, of complex **1**. These variations are accompanied by a concomitant increase of the absorbance at 1960 and 1790 cm^{-1} due to the carbonyl stretching vibrations of **2** and free succinic anhydride, respectively.

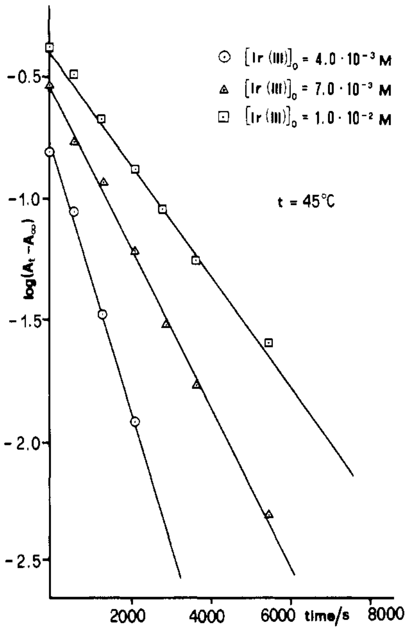


Figure 1. Semilogarithmic plot of the disappearance of complex **1** at various initial concentrations.

(2) Longato, B.; Bresadola, S. *Inorg. Chem.* **1982**, *21*, 168.
(3) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838.
(4) Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227.
(5) Basato, M.; Morandini, F.; Longato, B.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 649.

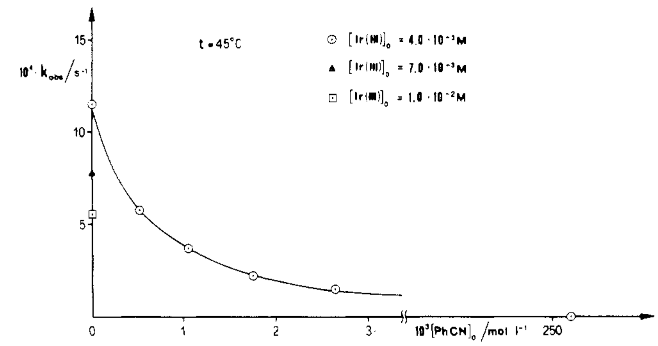


Figure 2. Dependence of k_{obsd} on the initial concentration of PhCN and of complex **1**.

This reaction follows a first-order rate law in complex concentration. In fact good linear relationship (>2–3 half-lives) are obtained by plotting log ($A_t - A_\infty$) vs. time, where the absorbances can be either those of the reagent or those of the products. In addition the k_{obsd} values determined from these semilogarithmic plots (usually related to the absorbance at 1760 cm^{-1}) increase as the initial concentration of **1** decreases (Figure 1).

Addition of PhCN to DCE solutions of **1**, though not effecting the reaction pattern of eq 1, drastically slows down the reaction rate, which still remains first order in complex concentration. The dependence of k_{obsd} on added PhCN is shown in Figure 2. Thus, the value of k_{obsd} for $[PhCN]_0 = 5.0 \times 10^{-4}$ mol dm^{-3} at 45 °C is reduced to about 50% of the value observed in absence of added PhCN, and the reductive-elimination reaction is completely inhibited by PhCN concentration about 10^{-1} mol dm^{-3}.

Moreover, by addition of PPh_3 to DCE solutions of **1**, the spectral pattern of the reaction products is modified and the reaction appears no longer first order. In fact, beside the absorption at 1790 cm^{-1} due to the free succinic anhydride, the ν(CO) absorption attributable to the terminal carbonyl of the iridium(I) product is centered at 1960 cm^{-1}. This value is consistent with the formation of the bis(phosphino) complex Ir(σ-carb)(CO)$(PPh_3)_2$.[6]

In this case a marked curvature of the semilogarithmic plots is observed. Thus, when a 10-fold excess of PPh_3 is added to **1**, the initial rate, which is roughly the same as in absence of added PPh_3, is reduced to ca. $^1/_3$ at half-reaction.

Finally, addition of $[PPh_3] = 4.0 \times 10^{-2}$ mol dm^{-3} to a DCE solution of **1** containing $[PhCN] = 1.0 \times 10^{-3}$ mol dm^{-3} produces a slight curvature of the semilogarithmic plot. The initial rate is the same as in the absence of PPh_3, indicating that, at least at the beginning of the reaction, there is no additional phosphine effect to that exhibited by PhCN on the reaction rate.

All the kinetic parameters of this reductive elimination are collected in Table I.

Carbonylation Reaction of Complex 1. Complex **1** reacts with CO, in DCE solution at room temperature, to give the dicarbonyl derivative Ir(H)[σ-CHCH$_2$C(O)OC(O)](σ-carb)$(CO)_2(PPh_3)$ (**3**) according to eq 2.

$$\mathrm{Ir(H)[\sigma\text{-}\overline{CHCH_2C(O)OC(O)}](\sigma\text{-}carb)(CO)(PhCN)(PPh_3) + CO \rightarrow \underset{\mathbf{3}}{Ir(H)[\sigma\text{-}\overline{CHCH_2C(O)OC(O)}](\sigma\text{-}carb)(CO)_2(PPh_3)} + PhCN} \quad (2)$$

Under a CO atmosphere, this reaction is quantitative and the carbonylation product **3** is stable toward the reductive elimination.

The rate of the carbonylation reaction has been determined by following the increase in the absorbance of the peak at 2095 cm^{-1}. The partial overlap of the band at 2050 cm^{-1} of **3** with the band at 2045 cm^{-1} due to **1** has prevented the determination of the reaction rate by following the disappearance of the reagent as in the previous case. The reaction is essentially instantaneous at 20 °C (1 atm of CO). Addition of PhCN affects only the reaction rate, which is markedly lowered. For $[PhCN] \leq 1.0 \times 10^{-1}$ mol dm^{-3}, a good linearity of the semilogarithmic plots is observed. The values of k_{obsd} so determined are proportional to the reciprocal of the PhCN concentration. Thus, the k_{obsd} value (20 °C, $[\mathbf{1}]_0 = 4.0 \times 10^{-3}$ mol dm^{-3}) is 7.7×10^{-4} s^{-1} for $[PhCN] = 5.0 \times 10^{-2}$ mol dm^{-3} and 4.1×10^{-4} s^{-1} for $[PhCN] = 1.0 \times 10^{-1}$ mol dm^{-3}. These values can be compared with the upper limit value of $k_{obsd} \geq 1 \times 10^{-2}$ s^{-1} evaluated from a kinetic run in the absence of added PhCN.

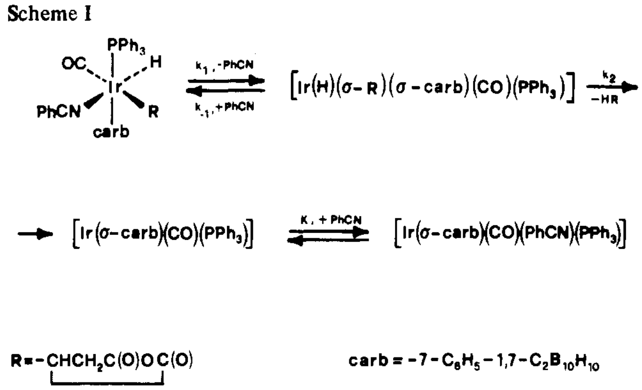
(6) Longato, B.; Morandini, F.; Bresadola, S. *Inorg. Chem.* **1976**, *15*, 650.

Table I. Kinetic Data of the Reductive-Elimination Reaction Ir(H)[σ-CHCH$_2$C(O)OC(O)](σ-carb)(CO)(PhCN)(PPh_3) → Ir(σ-carb)(CO)(PhCN)(PPh_3) + CH$_2$CH$_2$C(O)OC(O) in 1,2-Dichloroethane

T/°C	[1]/mol dm^{-3}	[PhCN][a]/mol dm^{-3}	k_{obsd}/s^{-1}
35	4.00×10^{-3}	0.00	3.04×10^{-4}
35	7.00×10^{-3}	0.00	2.18×10^{-4}
35	1.00×10^{-2}	0.00	1.44×10^{-4}
35	4.00×10^{-3}	4.00×10^{-4}	1.20×10^{-4}
35	4.00×10^{-3}	9.95×10^{-4}	6.15×10^{-5}
35	4.00×10^{-3}	1.50×10^{-3}	4.41×10^{-5}
35	4.00×10^{-3}	7.00×10^{-3}	9.06×10^{-6}
40	4.00×10^{-3}	0.00	5.25×10^{-4}
40	4.00×10^{-3}	0.00[b]	2.31×10^{-4} [c]
40	7.00×10^{-3}	0.00	3.72×10^{-4}
40	1.00×10^{-2}	0.00	2.57×10^{-4}
40	4.00×10^{-3}	4.05×10^{-4}	2.50×10^{-4}
40	4.00×10^{-3}	1.00×10^{-3}	1.43×10^{-4}
40	4.00×10^{-3}	1.00×10^{-3} [b]	1.41×10^{-4} [c]
40	4.00×10^{-3}	1.52×10^{-3}	9.71×10^{-5}
40	4.00×10^{-3}	2.03×10^{-3}	7.80×10^{-5}
45	4.00×10^{-3}	0.00	1.15×10^{-3}
45	7.00×10^{-3}	0.00	7.70×10^{-4}
45	1.00×10^{-2}	0.00	5.50×10^{-4}
45	4.00×10^{-3}	5.25×10^{-4}	5.77×10^{-4}
45	4.00×10^{-3}	1.05×10^{-3}	3.73×10^{-4}
45	4.00×10^{-3}	1.75×10^{-3}	2.26×10^{-4}
45	4.00×10^{-3}	2.64×10^{-3}	1.52×10^{-4}

[a] Concentration of added PhCN. [b] $[PPh_3] = 4.00 \times 10^{-2}$ mol dm^{-3}. [c] Value obtained by extrapolation of the curve log ($A_t - A_\infty$) vs. time in correspondence of the first half-life.

Scheme I



Discussion

The observed kinetic behavior is consistent with the reaction mechanism in Scheme I.

According to this scheme, reaction 1 occurs through a preliminary PhCN dissociation (k_1) to give the five-coordinate species Ir(H)[σ-CHCH$_2$C(O)OC(O)](σ-carb)(CO)(PPh_3). This undergoes intramolecular reductive elimination of succinic anhydride with formation of the three-coordinate complex Ir(σ-carb)(CO)(PPh_3), which in turn reacts with PhCN to generate the four-coordinate iridium(I) complex Ir(σ-carb)(CO)(PhCN)(PPh_3).

When the five-coordinate intermediate is considered as a reactive species to which it is possible to apply the steady-state treatment, the observed rate of the disappearance of **1** takes the form of eq 3.

$$k_{obsd} = k_1 k_2/(k_{-1}[PhCN] + k_2) \quad (3)$$

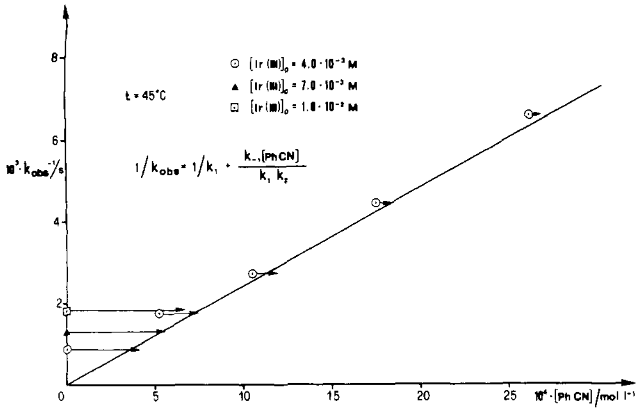


Figure 3. Data of Figure 2 rearranged according to eq 5 (see text). The horizontal arrows represent the additional concentration of PhCN derived from dissociation of complex **1**.

This rate equation is qualitatively consistent with the inhibiting effect played by PhCN. Moreover, the dependence of k_{obsd} on the initial complex concentration is consistent with the fast PhCN dissociation equilibrium (Scheme I). This equilibrium realizes in solution a benzonitrile concentration that increases as the initial complex concentration is increased. Furthermore, the observed good linearity of the semilogarithmic plots indicates that the concentration of PhCN is constant during the reaction. This observation can be explained by assuming that the dissociation constant of **1** ($K_d = k_1/k_{-1}$, mol dm^{-3}) has a value very close to that of product **2** (K). In addition, the rate-inhibiting effect and the scarce linearity of the semilogarithmic plots observed in the presence of PPh_3 are consistent with this mechanism. In this case the added PPh_3 substitutes the PhCN ligand in the reaction product **2** (eq 4), and as a consequence, during the reaction there is a progressive accumulation of free PhCN that decreases the reaction rate.

$$Ir(\sigma\text{-carb})(CO)(PhCN)(PPh_3) + PPh_3 \rightleftarrows Ir(\sigma\text{-carb})(CO)(PPh_3)_2 + PhCN \quad (4)$$

To verify the quantitative agreement of the kinetic data with the proposed mechanism, eq 3 can be rearranged in the form

$$1/k_{obsd} = 1/k_1 + k_{-1}[PhCN]/k_1k_2 \quad (5)$$

This means that a linear relationship is expected by plotting the reciprocal of the k_{obsd} values against [PhCN]. Figure 3 shows the data of Figure 2 rearranged according to eq 5. It appears that only for [PhCN] $\geq$ ca. 10^{-3} mol dm^{-3} a linear relation is verified. At lower [PhCN] a marked deviation from the linearity is observed according to k_{obsd} values lower than expected on the basis of the added PhCN. This behavior can be explained on consideration that only at higher concentration of added PhCN the additional contribution of PhCN due to the dissociation of complex **1** is negligible.

In order to linearize the function in the concentration range, we corrected all [PhCN] by adding the contribution due to PhCN dissociation from **1**. By an iterative method we could determine the value of K_d that gave the best linear fit. In Figure 3, these additional contributions are indicated with horizontal arrows defined by assuming a K_d value of 4.7×10^{-5} mol dm^{-3} at 45 °C. The resulting good linearity supports this treatment of the kinetic data.

The intercept of this straight line ($1/k_1$) has a value very close to 0, so indicating a very high rate for the dissociation of PhCN from complex **1**. This observation is confirmed by an independent study on the carbonylation reaction of complex **1** (eq 2). In fact, the inverse dependence of k_{obsd} on the concentration of added PhCN suggests that also the carbonylation reaction occurs through a PhCN dissociative mechanism, which likely involves the same five-coordinate intermediate as in the reductive-elimination reaction. Moreover, the very high reaction rate observed in absence of added PhCN clearly indicates that this PhCN dissociation rate (k_1) is very high.

Table II[a]

T/°C	10^5K ($=k_1/k_{-1}$)/ mol dm^{-3}	k_1k_2/k_{-1}/ mol dm^{-3} s^{-1}	10^3k_2/ s^{-1}
35	1.4	0.62×10^{-7}	4.46
40	3.0	1.59×10^{-7}	5.26
45	4.7	4.35×10^{-7}	9.19

[a] $\Delta H°$ ($=\Delta H_1{}^* - \Delta H_{-1}{}^*$) = ca. 100 kJ mol^{-1}; $\Delta S°$ ($=\Delta S_1{}^* - \Delta S_{-1}{}^*$) = ca. 230 J K^{-1} mol^{-1}; $\Delta H_1{}^* + \Delta H_2{}^* - \Delta H_{-1}{}^* = 156 \pm 5$ kJ mol^{-1}; $\Delta S_1{}^* + \Delta S_2{}^* - \Delta S_{-1}{}^* = 121 \pm 17$ J K^{-1} mol^{-1}; $\Delta H_2{}^*$ = ca. 56 kJ mol^{-1}; $\Delta S_2{}^*$ = ca. -109 J K^{-1} mol^{-1}.

The equilibrium and activation parameters calculated according to the mechanism depicted in Scheme I are reported in Table II.

The values of the dissociation constant (K) are in the range $(1.4\text{–}4.7) \times 10^{-5}$ mol dm^{-3} to which correspond a dissociation degree of 6–10% at 45 °C for a solution 4×10^{-3} mol dm^{-3} of **1**.[7]

The thermodynamic values ($\Delta H°$ = ca. 100 kJ mol^{-1}; $\Delta S°$ = ca. 230 J K^{-1} mol^{-1}) for this dissociative equilibrium are typical of a process that increases the total number of moles. Comparison of these values with those obtained[5] in the PPh_3 dissociation equilibrium from the iridium(III) derivative Ir(H)(Cl)(σ-carb)(CO)$(PPh_3)_2$ ($\Delta H°$ = 52 K J mol^{-1}; $\Delta S°$ = 65 J K^{-1}mol^{-1}) indicates that the dissociation of PhCN is favored and this is mainly due to a more favorable entropic variation.

The values of the complex rate function k_1k_2/k_{-1} do not give any direct information on the intimate reaction mechanism. However, on consideration that the dissociation constant K_d is the ratio k_1/k_{-1}, it is possible to determine an approximate value for k_2, i.e., the specific rate constant of the reductive elimination of succinic anhydride from the five-coordinate intermediate. The k_2 values are in the range $(4.46\text{–}9.19) \times 10^{-3}$ s^{-1} for the temperature range 35–45 °C.

Values of specific rate constants for reductive elimination from analogous hydrido alkyl intermediates are unknown. Only for the closely related complex Ir(H)(Cl)(σ-carb)(CO)(PPh_3), which eliminates H-carb, very similar values have been found.

A better insight into the reactivity of the intermediate Ir(H)[σ-$\overline{CHCH_2C(O)OC(O)}$]($\sigma$-carb)(CO)$(PPh_3)$ can be gained by a rough evaluation of the specific rate constants for the addition of neutral ligands (L = PhCN, CO, PPh_3). At 20 °C the specific reaction rate for the addition of neutral ligands to the five-coordinate intermediate are as follows: PhCN, $k \geq 2.5 \times 10^3$ mol dm^{-3} s^{-1}; CO, $k \simeq 2 \times 10^3$ mol dm^{-3} s^{-1}; PPh_3, $k \simeq 0$ mol dm^{-3} s^{-1}.[8] These values indicate that addition of the small molecules PhCN or CO is very fast and

(7) These values imply an appreciable concentration of the five-intermediate complex in solution, so that the steady-state treatment could be not completely justified. However, if we consider a fast equilibrium between **1** and the five-intermediate, followed by the reductive-elimination step (k_1, $k_{-1} \gg k_2$), a rate low is obtained that is consistent with the observed kinetic behavior. Furthermore, this rate law, under the experimental conditions, takes the same form as in the steady-state treatment.

(8) The data are derived as follows: (i) for PhCN and CO, from the k_{obsd} values of the carbonylation reaction $k_{obsd} = k_1k[CO]/(k[CO] + k_{-1}[PhCN])$ by using a $k_1/k_{-1} = K_d$ value extrapolated from the data at 35–45 °C for the reductive-elimination reaction; (ii) for PPh_3, from the observation of the negligible effect of added PPh_3 on the initial rate of the reductive-elimination reaction. Carbon monoxide solubility data from: "International Critical Tables"; McGraw-Hill: New York, 1929; Vol. III, p 265.

competes effectively with the reductive-elimination process. For example k_2 is about 10^{-6} times lower than the rate of CO addition. Bulkier ligands such as PPh_3 are substantially unreactive toward the addition, owing to the steric crowding around the metallic center.

The activation parameters for the reductive-elimination process show a rather low activation enthalpy ($\Delta H_2^* = 56$ kJ mol^{-1}) and negative activation entropy ($\Delta S_2^* = -109$ J K^{-1} mol^{-1}).

The evaluation of the transition metal–carbon single-bond energies is a rather controversial matter, and ranges from 160–350[9] and 80–120 kJ mol^{-1} [10] have been reported. For the metal–hydride bond the dissociation energy is about 240 kJ mol^{-1}.[11]

In spite of the large approximation in the evaluation of the energies involved in the dissociation of H and alkyl group from a metal center, the low ΔH^* value obtained in this study clearly indicates that the reductive elimination of succinic anhydride from the five-coordinate hydrido alkyl intermediate is a concerted process.

The negative value of the activation entropy is not common for a reductive-elimination process. However, it should be pointed out that the positive values reported in the literature usually refer to "observed rates" of reductive-elimination processes. These rates result from a series of elementary steps, and in particular they contain the kinetic term relative to a preliminary neutral ligand dissociation from the complex for which a largely positive activation entropy is expected. Moreover, quite negative activation entropy (−125 J K^{-1} mol^{-1}) was found in the "direct" reductive elimination of C_2H_6 from *fac*-[PtI$(CH_3)_3$(dppe)].[12] Thus, the combination of the values of the activation parameters observed in our case seems to suggest that the Ir–H and Ir–C bond breaking is limited in the transition state and at the same time the two ligand are forced away from their equilibrium positions to mutually interact. In this vision the drawing force of the reductive-elimination process is the incipient formation of the strong C–H bond of the product. A similar preliminary dissociation of a neutral ligand (PPh_3) was found in the reductive elimination of H-carb from hydrido complex Ir(H)(Cl)(σ-carb)(CO)$(PPh_3)_2$. However, in this case the activation parameters for the carborane reductive elimination from a five-coordinate hydrido carboranyl intermediate indicate a quite different intimate mechanism. The activation enthalpy is fairly high (160 kJ mol^{-1}) and the activation entropy (213 J K^{-1} mol^{-1}) largely positive. As a consequence, the activated state should imply a pronounced bond breaking that increases the disorder of the system. The carborane elimination process appears therefore little concerted; i.e., there is a scarce contribution of the process of H-carb bond formation to the energy balance. This interpretation is also consistent with the acidic character shown by the C–H bond in the H-carb molecule.

Conclusion

It seems common behavior in most *intramolecular* reductive-elimination reactions involving C–H and C–C bond formation that a preliminary dissociation of a neutral ligand is necessary to decrease the activation energy of this process,[12] and indeed this is the only behavior observed in the case of neutral octahedral complexes.[4] In general, hydrido alkyl complexes may be related to their scarce dissociation to give the reactive five-coordinate intermediate. Thus, the presence of labile auxiliary ligands in the coordination sphere of the metal should strongly favor the process of alkane reductive elimination.

Registry No. 1, 92282-17-2; **2**, 70700-96-8; **3**, 92184-39-9; Ir(σ-carb)(CO)$(PPh_3)_2$, 57527-11-4; Ir(H)(Cl)(σ-carb)(CO)$(PPh_3)_2$, 92282-18-3; Ir(H)[σ-$CHCH_2C$(O)OC(O)](σ-carb)(CO)(PPh_3), 92184-40-2; CH=CHC(O)OC(O), 108-31-6; CH_2CH_2C(O)OC(O), 108-30-5.

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