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Nitrile–Iridium(I) Complexes, 1-[Ir(CO)(RNC)(PPh$_3$)]-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$): Ligand Substitution and H_2 Oxidative Addition Reactions

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Treatment of trans-*[Ir(CO)(PPh$_3$)$_2$Y], Y = -7-C$_6$H$_5$-1,7-B$_{10}$C$_2$H$_{10}$, with RCN (R = CH$_3$, C$_6$H$_5$) in solution affords neutral complexes of general formula [Ir(CO)(RCN)(PPh$_3$)Y] which were isolated as yellow crystals. These complexes readily undergo substitution reactions with CO and phosphines to give neutral complexes which have been characterized by ir and ^{1}H nmr spectroscopy. The four-coordinate nitrile complexes add oxidatively molecular hydrogen giving octahedral adducts which readily undergo nitrile ligand substitution reactions with carbon monoxide and phosphines. The stereochemistry of*

TABLE I. Analytical (%) and I.r. (cm^{-1}, Nujol) Data for the Prepared Iridium-Carborane Complexes.

Complex[a]	M.P. (°C)[b]	Color	Found (Calcd.)			I.R. bands[c]		
			C	H	N	ν(CO)	ν(CN)	ν(Ir–H)
[Ir(CO)(CH$_3$CN)LY], (*2a*)	174	yellow	47.88 (47.69)	4.07 (4.03)	1.88 (1.62)	1982 vs	2300 vw 2320 vw	
[Ir(CO)(C$_6$H$_5$CN)LY], (*2b*)	191	yellow	50.97 (50.73)	4.08 (4.38)	1.75 (1.74)	1980 vs	2258 w	
[Ir(CO)$_2$L$_2$Y], (*3*)	111	orange	56.34 (55.68)	4.98 (4.57)		1998 s, 1940 vs		
[Ir(CO)$_3$LY], (*4*)	138	white	45.96 (45.78)	3.99 (3.98)		2060 w, 1980 s, 1970 s		
[Ir(CO)(Dpe)Y], (*5*)	150	orange	51.02 (50.16)	4.81 (4.69)		1983 vs		
[IrH$_2$(CO)(Dpe)Y], (*6*)	212	white	50.16 (50.05)	4.95 (4.92)		1997 vs		2122s, 2084 s
[IrH$_2$(CO)(CH$_3$CN)LY], (*7a*)	84	white	46.92 (46.76)	4.60 (4.73)	1.76 (1.88)	1992 vs	n.d.;	2235 m, 2119 s
[IrH$_2$(CO)(C$_6$H$_5$CN)LY], (*7b*)	160	white	50.28 (50.60)	4.26 (4.62)	1.61 (1.73)	1991 vs	2278 vw	2114 s, 2110 s
[IrH$_2$(CO)$_2$LY], (*9*)	156	white	45.95 (45.60)	4.40 (4.47)		2061 vs 2023 vs		2154 s, 2132 s

[a] L = PPh$_3$; Dpe = Ph$_2$P(CH$_2$)$_2$PPh$_2$; Y = -7-C$_6$H$_5$-1,7-B$_{10}$C$_2$H$_{10}$. [b] All compounds melt with decomposition in a capillary tube sealed under vacuum. Uncorrected values. [c] Key: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; n.d., not detected.

the resulting octahedral complexes has been assigned by a combination of ir and nmr spectroscopy.

Introduction

Recently we have reported that the stereochemical course of the oxidative addition of H_2 to *trans*-[Ir(CO)$(PPh_3)_2$Y], Y = -7-C_6H_5-1,7-$B_{10}C_2H_{10}$, complex *1*, is solvent-dependent [1]. Particularly, when the reaction of *1* with H_2 is carried out in acetonitrile solution a unique isomer of *cis*-addition having the two phosphine ligands in mutual *cis* positions was quantitatively obtained. This unusual stereochemical course together with the observation that the oxidative addition of HX (X = Cl, Br) to *1* in acetonitrile and benzonitrile solutions gives neutral nitrile adducts of iridium(III) of general formula [Ir(H)X(CO)(RCN)(PPh_3)Y] [2], prompted us to study the reaction of *1* with acetonitrile and benzonitrile. Thus, we have obtained the first examples of neutral four-coordinate iridium(I) complexes containing a nitrile ligand, [Ir(CO)(RCN)(PPh_3)Y], whose characterization is reported. The reactions of these square-planar nitrile complexes of iridium(I) with molecular hydrogen and the investigation on ligand substitution reactions of the resulting octahedral adducts with carbon monoxide and phosphines are also described. From the obtained results, the nitrile ligands appear to be more readily replaced by other ligands in the iridium(III) complexes than in the iridium(I) complexes.

Results and Discussion

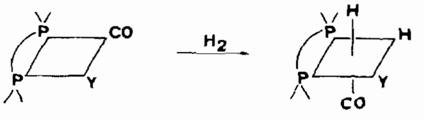
The complex *trans*-[Ir(CO)$(PPh_3)_2$Y], Y = -7-C_6H_5-1,7-$B_{10}C_2H_{10}$, *1*, reacts with RCN (R = CH_3, C_6H_5) at room temperature to give monophosphino nitrile iridium(I) complexes, *2a* and *2b* (Table I), of general formula [Ir(CO)(RCN)(PPh_3)Y], eq. 1:

$$\underset{1}{trans\text{-}[\mathrm{Ir(CO)(PPh_3)_2Y}]} + \mathrm{RCN} \rightleftharpoons \underset{2a\ \text{and}\ 2b}{[\mathrm{Ir(CO)(RCN)(PPh_3)Y}]} + \mathrm{PPh_3} \qquad (1)$$

This reaction is reversed by addition of free triphenylphosphine and an equilibrium constant K = 1.6 for the complex *2b* (RCN = C_6H_5CN) was found at 30 °C by ν(CN) absorption measurements. This value indicates that the iridium(I) displays comparable affinity towards both the labile ligands, as a result of a combination of steric and electronic factors which are not readily separable. The infrared spectra of *2a* and *2b* (Table I) exhibit the ν(CO) absorptions *ca.* 10–12 cm^{-1} higher than complex *1*, 1-[Ir(CO)$(PPh_3)_2$]-7-C_6H_5-1,7-(σ-$B_{10}C_2H_{10}$), (ν(CO), Nujol, 1970 cm^{-1}) and the ν(CN) bands increased slightly compared to the CN frequencies in the free nitriles in common with most nitrile complexes [3]. The rise in the ν(CO) frequencies observed for these nitrile complexes could indicate that the RCN ligands are weaker σ-donors and/or better π-acceptors than the PPh_3 ligand. However, it is to be noted that these ν(CO) vibrational frequencies are dependent on the symmetry of the related complexes which places a severe limitation to their usefulness, also on considering that these complexes contain a bulky carborane anionic ligand bound to the metal atom. The increase in ν(CN) upon coordination is in keeping with poor π-backbonding to the nitrile.

The ^1H nmr spectrum ($CDCl_3$) of complex *2a* exhibits the nitrile methyl proton resonance as a doublet centered at τ 8.40 with J_{PH} = 1.8 Hz. This resonance appears slightly upfield from free acetonitrile (singlet at τ 8.20). The occurrence of the observed long-range P–H coupling in the complex *2a* is not wholly convincing evidence for a *trans* combination of CH_3CN and PPh_3 in this square-planar complex. In fact, even though the cation $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ containing the acetonitrile ligand *cis* to the coordinated phosphines shows the methyl proton resonance as a singlet at τ 9.40 [4], coupling between methyl protons of a CH_3CN ligand and phosphorus nuclei of coordinated phosphines has been reported [5] for some platinum complexes in which the nitrile and phosphine ligands are mutually *cis*. Thus, on the basis of the obtained ir and ^1H nmr data it is not possible to establish unequivocally the stereochemistry of *2a* and *2b* and further work is required.

On treating solutions of *2a* and *2b* with the bidentate ligand Dpe, $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$, facile and irreversible displacement of both RCN and PPh_3 ligands occurs to give the four-coordinate complex *5*, [Ir(CO)(Dpe)Y], which was isolated as orange crystals. This complex shows poor solubility in the common organic solvents which prevented any further characterization. Complex *5* reacts with hydrogen in a benzene suspension yielding the white dihydrido complex *6* (Eq. 2).



(Eq. 2)

5 6

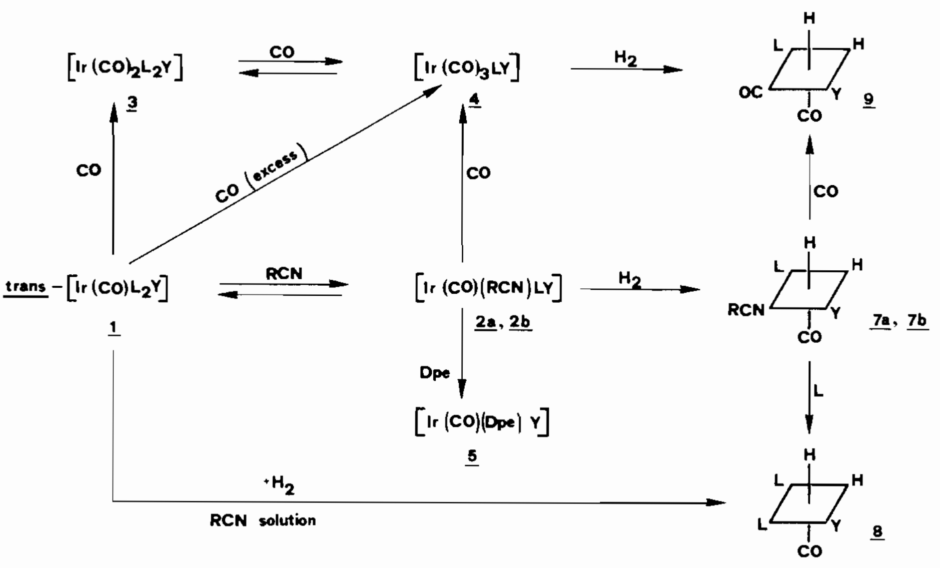
The adduct *6* appears to be a product of *cis*-addition. In fact the ^1H (hydride) nmr spectrum ($CDCl_3$) of *6* exhibits two doublets of doublets centered at τ 19.21 ($J_{P\text{–}H_{trans}}$ = 146.0 Hz; $J_{P\text{–}H_{cis}}$ = 14.2 Hz) and at τ 19.06 ($J_{P\text{–}H}$ = 17.8 Hz; $J_{P\text{–}H}$ = 17.9 Hz), respectively. The $J_{H\text{–}H}$ values appear to be lower than 0.9 Hz. This nmr pattern is in agreement with a structure for *6* in which two mutually *cis* hydrido ligands are *trans* to one P donor atom and to the CO group, respectively. The yellow solutions of *2a* and *2b* in benzene or 1,2-dichloroethane immediately turn colorless on bubbling CO through at room temperature to give the white crystalline five-coordinate tricarbonyl derivative, complex *4*. As shown in Scheme I, complex *4* can be also obtained on treating complex *1* with excess of CO (1 atm) at 25 °C in solution, taking care to perform any subsequent purification step under a CO atmosphere to prevent the formation of the dicarbonyl derivative *3*. Thus complex *4* is also formed when a benzene solution of the orange dicarbonyl complex *3* is treated with carbon monoxide at 25 °C and 1 atm (Eq. 3).

$$\underset{3}{[Ir(CO)_2L_2Y]} + CO \rightleftharpoons \underset{4}{[Ir(CO)_3LY]} + L \quad (3)$$

L = PPh_3: Y = -7-C_6H_5-1,7-$B_{10}C_2H_{10}$.

This carbonylation is reversed on flushing with dry nitrogen. Thus, when a benzene solution of *3* is treated with a CO atmosphere the color rapidly changes from orange to colorless. On sweeping with nitrogen the solution regains its initial orange color and by resaturation with carbon monoxide turns again colorless.

SCHEME I.



L = $P(C_6H_5)_3$; Dpe = $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$;
R = CH_3; C_6H_5; Y = -7-C_6H_5-1.7-$B_{10}C_2H_{10}$.

Complexes *2a* and *2b* stereospecifically undergo oxidative addition of hydrogen yielding the corresponding iridium(III) adducts *7a* and *7b*. The reaction is fast in benzene or trichloromethane solutions, but very slow in the solid state. The ^1H (hydride) nmr spectra ($CDCl_3$) of *7a* and *7b* show two doublets of doublets [complex *7a*: τ 17.15 (J_{P-H} = 20.1 Hz, J_{H-H} = 3.2 Hz) and τ 28.20 (J_{P-H} = 16.0 Hz, J_{H-H} = 3.2 Hz); complex *7b*: τ 17.04 (J_{P-H} = 19.7 Hz, J_{H-H} = 2.7 Hz) and τ 27.65 (J_{P-H} = 15.5 Hz, J_{H-H} = 2.7 Hz)] whose chemical shift and coupling constant values are in accordance with a structure in which the two mutually *cis* hydrido ligands are *trans* to CO and to RCN, respectively [1, 6, 7]. The nitrile ligands are irreversibly displaced from *7a* and *7b* by free triphenylphosphine to give stereospecifically the white dihydrido derivative of iridium(III) *8* containing two mutually *cis* phosphine ligands. This compound was previously obtained by us [1] on treating *1* with molecular hydrogen in acetonitrile solution. Thus, this result also explains the anomalous stereochemical course of the hydrogen oxidative addition reactions to the carborane bisphosphino iridium(I) complexes observed in acetonitrile solution, suggesting that these reactions proceed through solvent-containing intermediates when they are carried out in coordinating solvents. Furthermore, *7a* and *7b* react with CO (Scheme I) to give the dicarbonyl iridium(III) derivative *9* by displacement of the RCN molecule. This substitution reaction cannot be reversed by passing a stream of nitrogen in a 1,2-dichloroethane solution of *9* containing excess of free RCN. Complex *9* appears also to be the unique product of the reaction of *4* with hydrogen in benzene. The ^1H (hydride) nmr spectrum ($CDCl_3$) of *9* exhibits a doublet centered at τ 18.81 (J_{P-H} = 17.4 Hz) which suggests that the two hydrido ligands are mutually *cis* and both *trans* to the CO groups.

The stereochemistry of *8* and *9* indicates that these ligand substitution reactions occur with retention of configuration. In addition, the obtained results are testimony to the lower stability of the Ir—NCR bond in the iridium(III) derivatives compared to the iridium(I) complexes.

It is to be noted that the nitrile complexes (*2a*, *2b* and *7b* of Table I) exhibit higher ν(CN) frequencies compared to CN stretching frequencies in the free nitriles and that the increase is greater for the iridium(III) derivative *7b*. The latter result appears to be in contrast with the data reported in the literature for some hydrido complexes of iridium(III) containing coordinated nitriles, for which a considerable decrease of the ν(CN) frequencies ($\Delta\nu$(CN) ≈ -150 cm^{-1}) has been observed [8]. However, the rise in ν(CN) exhibited by the iridium–carborane complexes containing end-on coordinated nitriles is in agreement with an increase in the strength in the CN σ system as a consequence of electron pair donation [9]. In addition, a poorer π donation into antibonding orbitals of the coordinated benzonitrile molecule can be also invoked to justify the higher ν(CN) frequency shown by complex *7b*.

Experimental

Reagent grade solvents were further purified by standard methods and were dried and degassed before use. The complex *1*, 1-[Ir(CO)(PPh$_3$)$_2$]-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$), was prepared as previously reported [1]. All of the reactions involving iridium(I) complexes were carried out under argon. The ^{1}H nmr spectra were recorded at *ca.* 30 °C and at 60 MHz with the WP-60 FTNMR Bruker spectrometer. τ-values ± 0.02 ppm; J-values ± 0.2 Hz. ^{1}H shifts are relative to internal TMS (τ 10.00 ppm). Infrared spectra were obtained with a Perkin-Elmer Model 457 and calibrated against polystyrene film.

1-[Ir(CO)(RCN)(PPh$_3$)]-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$), 2a

Complex *1* (0.5 g) was dissolved in CH$_3$CN (2 ml) at room temperature. After few minutes a yellow microcrystalline precipitate was formed which was then separated by filtration, washed with n-hexane and dried under vacuum. The crude product was purified by recrystallization from benzene/n-hexane. The yield of pure yellow crystals of *2a* was 0.35 g (90%).

1-[Ir(CO)(C$_6$H$_5$CN)(PPh$_3$)]-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$), 2b

Complex *1* (1.0 g) was dissolved in C$_6$H$_5$CN (2 ml) at room temperature. After few minutes, 40 ml of n-hexane were added to the resulting solution and yellow crystals were then separated. The obtained solid was recrystallized from benzene/n-hexane to give 0.80 g (yield 96%) of yellow crystals of pure *2b*.

1-[Ir(CO)$_2$(PPh$_3$)$_2$]-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$), 3

A benzene (20 ml) solution of complex *1* (0.20 g) was stirred under CO atmosphere (1 atm) for five minutes at room temperature. A brief stream of nitrogen was then passed through the resulting solution. By addition of n-hexane a yellow-orange solid was precipitated which was purified by recrystallization from benzene/n-hexane to give orange crystals (0.15 g, 73%) of pure *3*.

1-[Ir(CO)$_3$(PPh$_3$)]-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$), 4

A stream of carbon monoxide was passed through a CH$_2$Cl$_2$ solution of complex *2a* (0.5 g). After 5 min addition of n-hexane to the resulting pale-yellow solution afforded a white precipitate which was separated and washed with n-hexane. The crude product was recrystallized from benzene/n-hexane under CO atmosphere. The yield of pure *4* was 0.3 g (60%). Following the same procedure, complex *4* was also obtained starting from the derivative *2b*.

1-[Ir(CO)(Dpe)]-7-C$_6$H$_5$-1, 7-(σ-B$_{10}$C$_2$H$_{10}$), 5

A suspension of *2a* or *2b* (0.62 mmol) in benzene (5 ml) was treated with an excess of (C$_6$H$_5$)$_2$P(CH$_2$)$_2$-P(C$_6$H$_5$)$_2$, Dpe (1.5 g, 3.7 mmol) in benzene (10 ml) at room temperature. After *ca.* 10 min an orange microcrystalline solid was formed which was filtered and washed with n-hexane. The poor solubility of the obtained solid prevented any further purification. The yield of crude orange product was 0.30 g (60%).

1-[IrH$_2$(CO)(Dpe)]-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$), 6

Hydrogen was bubbled into a suspension of complex *5* (0.20 g) in benzene (10 ml) at room temperature. The initial suspension gave a colorless solution in the course of *ca.* 1 min. Then, addition of n-hexane afforded a white product which was further purified by recrystallization from CH$_2$Cl$_2$/CH$_3$OH; yield 0.18 g (90%) of *6*.

1-[IrH$_2$(CO)(CH$_3$CN)(PPh$_3$)]-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$), 7a

Complex *2a* (0.3 g) was dissolved in CH$_2$Cl$_2$ (5 ml) and hydrogen was bubbled through the obtained solution at room temperature. The yellow solution immediately turned colorless. Addition of n-hexane caused precipitation of a white solid which was purified by recrystallization from benzene/n-hexane to give white crystals of pure *7a*; yield 0.28 g (93%).

1-[IrH$_2$(CO)(C$_6$H$_5$CN)(PPh$_3$)]-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$), 7b

This complex was obtained as above starting from *2b*. The crude product was recrystallized from benzene/n-hexane and a yield of 89% of white crystals of pure *7b* were obtained. The corresponding dideuterido complex was similarly prepared using deuterium.

1-$[IrH_2(CO)(PPh_3)_2]$-7-C_6H_5-$1,7$-$(\sigma$-$B_{10}C_2H_{10})$, 8

Free triphenylphosphine was added to benzene solutions of *7a* and *7b* at room temperature. Then, by addition of n-hexane to the resulting solutions white crystals of complex *8* was quantitatively obtained in both the cases. The crude precipitate was recrystallized from CH_2Cl_2/CH_3OH. *Anal.* Calcd. for $C_{45}H_{47}B_{10}OP_2Ir$: C, 55.95; H, 4.90. Found: C, 55.85; H, 4.98. mp 140° dec.

Infrared spectrum (cm^{-1}, Nujol): ν(CO) = 1987 s; ν(Ir–H) = 2196 w, 2138 s.

^1H (hydride) resonances in $CDCl_3$: doublets of doublets centered at τ 18.6 (J_{P-H} = 14.6; 22.4 Hz) and at τ 20.73 (J_{P-H} = 21.5, 144.2 Hz). Each peak of these signals is further split into two lines by H–H coupling (J_{H-H} = 2.7 Hz).

1-$[IrH_2(CO)_2(PPh_3)]$-7-C_6H_5-$1,7$-$(\sigma$-$B_{10}C_2H_{10})$, 9

Complex *9* was prepared by bubbling for few minutes either CO through benzene solutions of *7a* and *7b* or H_2 through a benzene solution of complex *4*. Then addition of n-hexane to the obtained reaction mixtures afforded a white precipitate which was separated by filtration and purified by recrystallization from CH_2Cl_2/n-hexane. White crystals of pure *9* were quantitatively obtained.

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7 The dideuterido complex corresponding to *7b* shows ν(CO) at 2020 cm^{-1} ($\Delta\nu$(CO) = +29 cm^{-1}) and ν(CN) at 2273 cm^{-1} ($\Delta\nu$(CN) = −5 cm^{-1}) in agreement with the expectation of CO *trans* to H in *7b* (see L. Vaska, *J. Am. Chem. Soc., 88,* 4100 (1966)).

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