8-OXYQUINOLATE IRIDIUM(I) COMPLEXES AND THEIR OXIDATIVE-ADDITION REACTIONS

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Summary

The novel sixteen-electron complex [Ir(Oq)(COD)] (Oq = 8-oxyquinolate; COD = 1,5-cyclooctadiene) adds monodentate phosphines, phosphites or activated olefins irreversibly to give pentacoordinate iridium(I) complexes of the type [Ir(Oq)(COD)L] (L = PPh_3, $P(OPh)_3$, maleic anhydride or tetracyano-ethylene). Reaction of [Ir(Oq)(COD)] with some diphosphines leads to substitution products of the general formula [Ir(Oq)(diphos)] (diphos = 1,2-bis-(diphenylphosphino)ethane or *cis*-1,2-bis(diphenylphosphino)ethylene). Carbon monoxide displaces the COD group from the complexes giving either [Ir(Oq)(CO)$_2$] or [Ir(Oq)(CO)L], and the latter undergo oxidative addition reactions with $SnCl_4$, Me_3SiCl, Me_3SnCl, MeI, allylbromide, PhCOCl, MeCOCl, Cl_2, Br_2, $TlCl_3$ and HCl leading to novel iridium(III) complexes.

Introduction

Although the synthesis, structure and reactivity of several rhodium 8-oxy-quinolate complexes has been studied in detail [1—4], the corresponding chemistry of iridium 8-oxyquinolate derivatives has been only briefly explored [1]. It is known [5,6] that the ability of d^8 complexes to undergo oxidative addition reactions is highly dependent upon the nature of the attached ligands. Thus, no oxidative addition is observed for neutral complexes containing salicylaldiminates [7].

In the present paper we report the synthesis and reactions of several 8-oxy-quinolate iridium complexes. In particular, the behaviour of [Ir(Oq)CO{P(*p*-R-C$_6$H$_4$)}$_3$] complexes is similar to that of Vaska's compound.

Results and discussion

Reactions of [Ir(μ-Cl)(COD)]$_2$ in oxygen-free methanol at room temperature with an equimolecular amount of sodium 8-oxyquinolate in water-methanol

TABLE 1

ANALYTICAL DATA FOR THE IRIDIUM(I) COMPLEXES

Complex	Colour	M.p. (°C)	Found(calcd.)(%)			Yield (%)	$\nu(CO)(CH_2Cl_2)$ (cm^{-1})
			C	H	N		
[Ir(Oq)(COD)] (I)	deep red	210—211	45.6 (45.9)	4.1 (4.1)	3.2 (3.1)	80—90	—
[Ir(Oq)(CO)$_2$](II)	black	—	32.4 (33.7)	1.8 (1.5)	3.4 (3.9)	70	2070 1986
[Ir(Oq)(COD)(mal)](III)	yellow	125—130(d)	46.7 (46.5)	4.2 (3.7)	2.4 (2.6)	80	—
[Ir(Oq)(COD)TCNE] (IV)	yellowish-brown	250	47.8 (48.2)	3.3 (3.2)	12.4 (12.2)	90	—
[Ir(Oq)(COD)(PPh$_3$)] (V) ^{a}	orange	139—140	59.6 (59.5)	4.9 (4.7)	2.2 (2.0)	82—92	—
[Ir(Oq)(COD){P(OPh)$_3$}] (VI)	orange	90—92	55.8 (55.7)	4.7 (4.4)	1.9 (1.8)	82	—
[Ir(Oq)(dppe)] (VII)	orange	170—173	56.0 (57.2)	4.7 (4.1)	1.8 (1.9)	89	—
[Ir(Oq)(dppen)] (VIII)	orange	190—192(d)	57.7 (57.3)	4.3 (3.8)	1.6 (1.9)	95	—
[Ir(Oq)(CO)(PPh$_3$)] (IX) ^{b}	orange	212—213	53.9 (53.7)	3.5 (3.4)	2.3 (2.2)	75	1945
[Ir(Oq)(CO){P(OPh)$_3$}] (X)	orange	164—165	49.7 (49.8)	3.3 (3.1)	2.3 (2.1)	80	1975
[Ir(Oq)(CO){P(4-MeOPh)$_3$}] (XI) ^{c}	orange	190—192	52.4 (51.9)	4.0 (3.8)	1.9 (1.9)	85	1945
[Ir(Oq)(CO){P(4-MePh)$_3$}] (XII) ^{c}	yellow-orange	132(d)	56.7 (55.8)	4.5 (4.1)	2.2 (2.1)	65	1947
[Ir(Oq)(CO){P(4-ClPh)$_3$}] (XIII) ^{c}	yellow-orange	190(d)	46.1 (46.4)	2.5 (2.5)	1.9 (1.8)	76	1950

^{a} Molecular weight = 550(706.8); ^{b} Molecular weight = 654(627); ^{c} $\Lambda_M = 0 \, \Omega^{-1} \, cm^2 \, mol^{-1}$.

solution give good yields of a deep red microcrystalline solid, which was identified as [Ir(Oq)(COD)] (I) (Oq = 8-oxyquinolate; COD = 1,5-cyclooctadiene) (Table 1). Attempts to recrystallize complex I give an impure compound similar to that obtained by reacting [Ir(Oq)(CO)$_2$] for several days with 1,5-cyclooctadiene in refluxing benzene, as previously described [1].

The ^{1}H NMR spectrum of complex I confirms its square-planar structure, the molecular plane being the only plane of symmetry. The ^{1}H NMR resonance of the CH$_2$ groups in COD is split into two multiplets of equal intensity, thus pointing to a different environment of the "inside" and "outside" protons. The different *trans*-influence of the N or O donor atoms leads to non-equivalence of the corresponding *trans*-olefinic protons. By analogy with ^{1}H NMR studies of related rhodium (olefin)(chelate) complexes [8], we assign the lower field (5.3τ) resonance to the olefinic protons *trans* to oxygen. This magnetic and chemical non-equivalence is not evidenced by the reactions of complex I with monodentate ligands, in which the diolefin is either completely displaced or remains attached to the iridium atom through both olefinic bonds.

Bubbling CO through a dichloromethane solution of complex I causes an instantaneous change in colour from orange to green, which is followed by the precipitation of black crystals, which were identified as the previously described [1] dicarbonyl [Ir(Oq)(CO)$_2$] (II) (ν(CO)) in CCl$_2$H$_2$: 2070s and 1986s cm^{-1}). The ready replacement of COD by carbon monoxide is in accord with the difficulty of the reverse reaction [1]. The COD ligand in complex I cannot be replaced at room temperature by ethylene, hexamethylbenzene or diphenylacetylene. However, olefins which are stronger π-acceptors, such as maleic anhydride or tetracyanoethylene, react with I giving the presumably penta-coordinated addition products [Ir(Oq)(COD)(olefin)]. Carbonylation of solutions of these complexes leads also in both cases to [Ir(Oq)(CO)$_2$], though the reactions are slower than with complex I.

The results are a consequence of the existence of a free coordination site in the sixteen-electron complex I, though not every ligand is capable of occupying this site. Thus, addition of tertiary phosphines or phosphites to a suspension of I in oxygen-free ether gives air-sensitive orange solutions, from which orange microcrystalline solids [Ir(Oq)(COD)L] can be isolated when L = PPh$_3$ (V) or P(OPh)$_3$ (VI), whereas when L = PEt$_3$, PBu$_3$, PMePh$_2$ or P(OMe)$_3$, non-crystallizable oils are obtained. Moreover, no reaction takes place when L = PCy$_3$, AsPh$_3$, py or PhCN.

Addition of diphosphines, such as 1,2-bis(diphenylphosphino)ethane (dppe) or *cis*-1,2-bis(diphenylphosphino)ethylene (dppen) to oxygen-free ether solutions of complex I leads to orange solutions, from which the complexes [Ir(Oq)(dppe)] (VII) or [Ir(Oq)(dppen)] (VIII) can be isolated by evaporating off the solvent. Analogous reactions with bis(diphenylphosphino)methane or 1,4-bis(diphenylphosphino)butane yield orange microcrystalline solids of as yet unknown structure.

Carbonylation of dichloromethane solutions of complexes of the type [Ir(Oq)(COD)L] also caused ready displacement of the COD group by CO (the resulting solutions show only a single absorption due to ν(CO) at ~1945 cm^{-1}), but the orange crystalline solids could only be isolated for L = PPh$_3$ (IX) and P(OPh)$_3$ (X).

TABLE 2

ANALYTICAL DATA FOR THE IRIDIUM(III) COMPLEXES

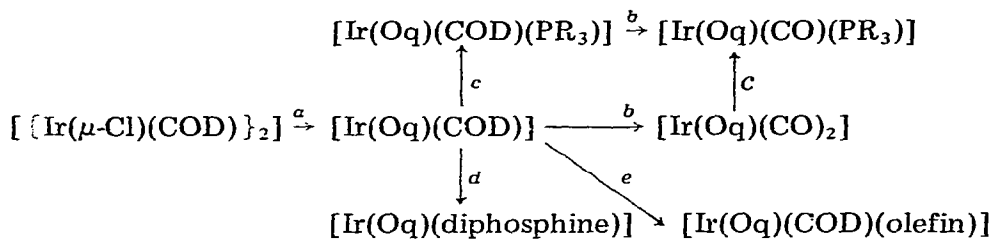| Complex	Found(calcd.)(%)			M.p. (°C)	$\nu(CO)(CH_2Cl_2)$ (cm^{-1})	Other IR bands
	C	H	N			
[Ir(COPh)Cl(Oq)(CO)PPh$_3$] (XIV)	54.7 (54.9)	4.1 (3.4)	1.7 (1.8)	165(d)	2050	ν(Ir—Cl): 245w ν(C=O): 1632s
[Ir(COMe)Cl(Oq)(CO)PPh$_3$] (XV)	49.2 (51.1)	3.6 (3.4)	2.0 (2.0)	145	2048	ν(Ir—Cl): 240w ν(C=O): 1655s
[Ir(COPh)Cl(Oq)(CO){P(4-MeOPh)$_3$}] (XVI) ^{a}	53.9 (53.2)	4.2 (3.7)	1.7 (1.6)	139(d)	2048	
[Ir(COPh)Cl(Oq)(CO){P(4-MePh)$_3$}] (XVII)	56.9 (56.4)	4.4 (4.0)	2.0 (1.7)	135(d)	2055	ν(C=O): 1640s
[Ir(COPh)Cl(Oq)(CO){P(4-ClPh)$_3$}] (XVIII)	50.1 (48.3)	3.2 (2.7)	2.1 (1.6)	194(d)	2058	ν(C=O): 1642s ν(Ir—Cl): 298m(br)
[IrMeI(Oq)(CO)PPh$_3$] (XIX)	45.0 (45.3)	3.1 (3.1)	1.8 (1.8)	246(d)	2028	ν(C=O): 1638s
[IrMeI(Oq)(CO){P(4-MeOPh)$_3$}] (XX) ^{a}	45.4 (44.8)	3.9 (3.7)	1.8 (1.7)	135(d)	2023	
[IrMeI(Oq)(CO){P(4-MeOPh)$_3$}] (XXI)	48.1 (47.4)	3.9 (3.7)	1.8 (1.7)	138(d)	2021	
[IrMeI(Oq)(CO){P(4-ClPh)$_3$}] (XXII)	41.0 (40.0)	2.5 (2.4)	1.9 (1.6)	222(d)	2031	
[IrBr(α-allyl)(Oq)(CO)PPh$_3$] (XXIII)	49.4 (49.8)	3.6 (3.5)	2.1 (1.9)	187—190(d)	2029	ν(C=C): 1618w
[IrBr(α-allyl)(Oq)(CO){P(4-MeOPh)$_3$}] (XXIV) ^{a}	49.0	4.0	1.8	131(d)	2026	ν(C=C): 1620w

Compound	C	H	N	m.p.	ν(CO)	
[IrBr(σ-allyl)(Oq)(CO){P(4-ClPh)₃}] (XXXVI)	44.2 (51.7) (43.7)	3.1 (4.1) (2.7)	1.7 (1.8) (1.6)	190(d)	2033	ν(C=C): 1622w
[IrCl(SnCl₃)(Oq)(CO)PPh₃] (XXVII)	37.6 (37.9)	2.6 (2.4)	1.7 (1.6)	>295	2063	ν(Ir—Cl): 297w ; ν(Sn—Cl): 356s, 344s
[IrCl(SnCl₃)(Oq)(CO){P(4-MeOPh)₃}] XXVIII	37.9 (38.1)	2.9 (2.8)	1.4 (1.4)	>290	2058	ν(Ir—Cl): 320(sh), 305w ; ν(Sn—Cl): 355(sh), 345s
[IrCl(SnCl₃)(Oq)(CO){P(4-MePh)₃}] (XXIX)	39.1 (40.1)	3.1 (2.9)	1.1 (1.5)	198(d)	2062	ν(Ir—Cl): 305(sh) ; ν(Sn—Cl): 340b
[IrCl(SnCl₃)(Oq)(CO){P(4-ClPh)₃}] (XXX)	36.1 (34.0)	2.5 (2.4)	—	295(d)	2064	ν(Ir—Cl): 305(sh), 280w ; ν(Sn—Cl): 340(br)
[IrCl(SnMe₃)(Oq)(CO)PPh₃] (XXXI)	45.0 (45.1)	3.5 (3.7)	1.8 (1.8)	>295	2048	
[IrCl(SnMe₃)(Oq)(CO){P(4-MeOPh)₃}] (XXXII)	43.9 (44.6)	3.9 (3.7)	1.5 (1.8)	>290	2051	
[IrCl(SiMe₃)(Oq)(CO)PPh₃] (XXXIII) [b]	49.0 (50.6)	3.4 (4.1)	2.0 (1.9)	155(d)	2038	ν(Ir—Cl): 253w
[IrCl(SiMe₂Cl)(Oq)(CO){P(4-MeOPh)₃}] (XXXIV) [c]	44.6 (46.8)	4.3 (3.9)	1.6 (1.6)	154	2047	ν(Ir—Cl): 305w, 268w
[IrCl(SiMe₃)(Oq)(CO){P(4-MePh)₃}] (XXXV)	52.8 (52.5)	5.1 (4.7)	2.0 (1.8)	180(d)	2048	ν(Ir—Cl): 315w, 305w
[IrCl(SiMe₃)(Oq)(CO){P(4-ClPh)₃}] (XXXVI)	45.4 (44.4)	3.0 (3.2)	1.5 (1.7)	157(d)	2039	ν(Ir—Cl): 250w
[IrCl₂(C₉Cl₆NO)(CO)PPh₃] (XXXVII)	37.5 (37.2)	2.5 (1.7)	1.3 (1.5)	>300	2070	ν(Ir—Cl): 340–300(br)
trans-[IrCl₂(Oq)(CO)PPh₃] (XXXVIII)	47.9 (48.2)	3.2 (3.0)	2.0 (2.0)	234–235	2068	ν(Ir—Cl): 334s
[IrBr₂(Oq)(CO)PPh₃](XXXIX)	42.8 (42.8)	3.0 (2.7)	1.7 (1.8)	—	2060	

[a] $\Lambda_M = 1\ \Omega^{-1}\ cm^2\ mol^{-1}$; [b] Molecular weight = 772(735.7); [c] $\Lambda_M = 22\ \Omega^{-1}\ cm^2\ mol^{-1}$.

_ A direct method for the synthesis of complexes of the type [Ir(Oq)(CO)L] (L = PPh$_3$ (IX), P(4-MeOPh)$_3$ (XI), P(4-MePh)$_3$ (XII) and P(4-ClPh)$_3$ (XIII)) can be proposed on the basis of the above-described reactions (see Scheme 1).

SCHEME 1

$$[Ir(Oq)(COD)(PR_3)] \xrightarrow{b} [Ir(Oq)(CO)(PR_3)]$$

$$\Big\uparrow c \qquad\qquad\qquad \Big\uparrow c$$

$$[\{Ir(\mu\text{-Cl})(COD)\}_2] \xrightarrow{a} [Ir(Oq)(COD)] \xrightarrow{b} [Ir(Oq)(CO)_2]$$

$$\Big\downarrow d \qquad\qquad \searrow e$$

$$[Ir(Oq)(diphosphine)] \xleftarrow{} [Ir(Oq)(COD)(olefin)]$$

[a] NaOq; [b] CO; [c] PR$_3$; [d] diphosphine = dppe or dppen; [e] olefin = maleic anhydride or tetracyanoethylene.

Thus, treatment of a tetrahydrofuran solution of [Ir(μ-Cl)(COD)]$_2$ with sodium 8-oxyquinolate leads to an intense red solution of [Ir(Oq)(COD)], which after addition of an equimolecular amount or a slight excess of the respective phosphine and subsequent bubbling of carbon monoxide turns orange; complexes of the type [Ir(Oq)(CO)L] can be isolated from the solution as orange microcrystalline solids in high yields.

The above reaction gives only one of the two possible isomers of [Ir(Oq)-(CO)L] (L = phosphine ligand) as can be seen from the presence of only one ν(CO) vibration, which falls between 1950 and 1945 cm^{-1}. Since the rhodium complex [Rh(Oq)(CO)PPh$_3$] [1], in which the phosphine group is known from an X-ray diffraction study to be *trans* to the heterocyclic nitrogen [2], shows the ν(CO) band at 1965 cm^{-1}, it can reasonably be assumed that the configuration of the iridium complex [Ir(Oq)(CO)L] is similar.

Oxidative addition reactions

Complexes of the type [Ir(Oq)(CO)L] can be regarded as formally derived from Vaska's complex [9] with the chlorine and phosphine ligands replaced by the 8-oxyquinolate group; their ν(CO) bands lie at even lower energies than in Vaska's complex (1965 cm^{-1}) [10]. Since the ν(CO) bands should give an indication of the nucleophility of an iridium carbonyl complex, it seemed of interest to explore the oxidative addition reactions of this family of compounds. We used several reagents regarded as standard for this type of reaction, along with others whose reactions with iridium(I) complexes have been little studied.

The reactions are generally so rapid that no kinetic studies could be carried out. As expected for this kind of reactions [10], the ν(CO) vibration of the oxidation products is shifted in every case towards higher energies relative to the parent compound (see Table 2).

Acyl halides react with [Ir(Oq)(CO)L] complexes to give the acyliridium-(III) derivatives [Ir(COR)Cl(Oq)(CO)L]. Though decarbonylation and insertion of CO into the R—metal linkage are common for rhodium acyl derivatives and less usual for iridium compounds [12,13] at room temperature, there was no indication of any decarbonylation of these new complexes.

The following data serve to elucidate the stereochemistry of this type of reaction. While the product of the addition of benzoyl chloride or acetyl chloride to complex IX shows the ν(Ir—Cl) band at 245 or at 240 cm^{-1} respectively (which according to ref. 12 indicates a *trans* disposition) benzoyl chloride adds *cis* to the complex [Ir(Oq)(CO) {P(4-ClPh)$_3$}] since the ν(Ir—Cl) band of the reaction product appears at 298 cm^{-1}, so that its chlorine ligand must be *trans* to CO. For the other two complexes the ν(Ir—Cl) bands could not be unambiguously assigned.

Alkyl halides such as methyl iodide or allyl bromide react with complexes of the type [Ir(Oq)(CO)L] to give [Ir(Me)I(Oq)(CO)L] or [IrBr(σ-allyl)(Oq)-(CO)L]. The reactions with allyl bromide lead to only one complex, in which the allyl group is σ-bonded to the iridium atom, as may be seen from the ν(C=C) band which is found at the expected location [14] at 1620 cm^{-1}. The reactions with methyl iodide yield a mixture of products, from which the required complex is obtained by recrystallization.

The sharpness of the single peak due to ν(CO) in the IR spectra of our complexes seems to point to the presence of only one isomer, but this should be regarded with reservation since the ν(Ir—Br) and ν(Ir—I) bands could not be detected.

Though oxidative addition reaction of organotin halides and organosilicon halides to platinum(0) complexes have been extensively studied [15], no such reactions with iridium(I) compounds have been reported. Tin tetrachloride reacts instantaneously with compounds of the type [Ir(Oq)(CO)L] to give complexes of the general formula [IrCl(SnCl$_3$)(Oq)(CO)L], whose IR spectra show two bands at 350—340 cm^{-1} (which in some cases overlap to give a single broad band), assignable to the SnCl$_3$ group. Another ν(Ir—Cl) band at approx. 300 cm^{-1} (see Table 2) corresponds to a Cl group *trans* to CO. Therefore, the oxidative addition of SnCl$_4$ to this family of complexes must be *cis*. In contrast to the reaction product from SnCl$_4$ with [IrCl(CO)(PPh$_3$)$_2$] [16], complexes XXVII—XXX show a single sharp ν(CO) band (both for the solids and their dichloromethane solutions). Possible oxidation-reduction transformations can therefore be ruled out.

The reactions of trimethyltin-chloride with complexes of the type [Ir(Oq)-(CO)L] are very much slower. In the absence of air they are complete only after 2—3 days, whilst in the presence of air the solution darkens at once and the reaction is complete in less than 1 hour. This suggests that a free radical mechanism probably operates in these cases [17]. The fact that no reaction takes place between hydrogen and [Ir(Oq)(CO)L] in dichloromethane at room temperature also points to this type of mechanism.

Chlorotrimethylsilane and dichlorodimethylsilane react with [Ir(Oq)(CO)L] to give [IrCl(SiMe$_3$)(Oq)(CO)L] and [IrCl(SiClMe$_2$)(Oq)(CO)L], respectively. The reaction mixtures show two bands of different intensities in the carbonyl region, thus suggesting the formation of two isomers. The isolated products also show two bands in the solid state, but only one in solution. This can probably be attributed to a splitting of the band in the solid state, but other reasons, such as the coexistence of more than one isomer, cannot be ruled out. Complexes XXXIII, XXXIV and XXXVI show the ν(Ir—Cl) band at lower frequencies, e.g. at 253 cm^{-1} for complex XXXIII. Because of the strong *trans*

influence of the SiR$_3$ group [18], this ligand must be *trans* to Cl, and the addition seems therefore to be fundamentally *trans* (except in complex XXXV).

Complexes with weak Ir—Si bonds [18,19,20] frequently undergo dissociation and would be expected to occur in the solutions of the iridium alkylsilane derivatives described above. Indirect evidence for this dissociation is the decomposition of the complexes upon attempting to recrystallize them. The ^{1}H NMR spectrum of complexes XXXIII shows several peaks in the 9—10τ range. If a solution of this complex is passed through a thin layer of alumina it is reduced to Ir^I and the parent complex IX is recovered.

The oxidative-addition of chlorine to [Ir(Oq)(CO)PPh$_3$] in dichloromethane at room temperature seems noteworthy. Thus, bubbling of Cl$_2$ through a solution of IX leads not only to the oxidation of the Ir^I complex, but also to halogenation of the aromatic rings of the 8-oxyquinolate ligand. The extent of this substitution depends upon the reaction conditions, but the reaction finally leads to a white solid of the formula {IrCl$_2$(C$_9$Cl$_6$NO)(CO)(PPh$_3$)] (XXXVII). Such perhalogenations have previously been reported: for example, that of the 8-oxyquinolate ligand in [Rh(Oq)(CO)PPh$_3$] [3] and that of the *o*-metallated phenyl group in a series of iridium triphenylphosphite complexes of the type [Ir{P(OC$_6$H$_4$)(OPh)$_2$} (COD) {P(OPh)$_3$}] [21]. [IrCl$_2$(Oq)(CO)PPh$_3$] (XXVIII) can be obtained by reacting complex IX with TlCl$_3$, though the result is strongly influenced by the ratios of reagents used. Reaction with a large excess of TlCl$_3$ leads quickly to a green solid which contains a mixture of *cis*- and *trans*-[IrCl$_2$(Oq)(CO)PPh$_3$], along with other compounds. The reaction of stoichiometric amounts of the reagents is slow and gives a cream-coloured solid containing thallium, which must be an intermediate product. *trans*-[IrCl$_2$(Oq)-(CO)PPh$_3$] (ν(CO): 2068 cm^{-1}; ν(Ir—Cl): 334 cm^{-1}) along with a small amount of the *cis*-isomer (ν(CO): 2080 cm^{-1}; ν(Ir—Cl): 290, 280 cm^{-1}) can be obtained in good yield by prolonged reaction of IX with a slight excess of TlCl$_3$. The isomers formed can be separated by fractional crystallization.

The reaction of complex IX with the stoichiometric amount of Br$_2$ leads to [IrBr$_2$(Oq)(CO)PPh$_3$] (XXXIX). Hydrogen chloride reacts with IX to give [IrHCl(Oq)(CO)PPh$_3$] which can be isolated as an off-white solid (ν(Ir—H): 2270 cm^{-1}; ν(CO): 2042 cm^{-1}). Owing to its instability at room temperature no satisfactory analytical data could be obtained. The addition is probably *cis*, although several isomers in which Cl is either *trans* to CO (ν(Ir—Cl): 315 cm^{-1}) or *trans* to PPh$_3$ (ν(Ir—Cl: 285 cm^{-1}) are usually obtained in approx. equivalent amounts.

The iridium(I) and -(III) monocarbonyls are respectively orange and, yellow in agreement with the lack of intermolecular Ir—Ir interactions [1] in the solid state for obvious steric reasons.

No significant hydrogenation (1 atm H$_2$) of 1-heptene takes place in dichloromethane at room temperature in the presence of complex IX as catalyst.

IR spectra

The coordination of the 8-oxyquinolate group [22,23] can clearly be inferred from the ν(CO) at 1325 cm^{-1} and the ν(CN) at ~1110 cm^{-1}. The location of these absorptions does not vary with the oxidation state of the central atom.

Though the small fluctuations of the position of the ν(CO) band for complexes IX, XI, XII and XIII are within the experimental error, they are larger in the oxidation products than in the starting compounds (see Table 2). ν(CO) decreases, as expected, with increasing basicity of the relevant phosphine. The influence of the introduced ligand may also clearly be seen from the ν(CO) stretching vibrations. Despite the influence of the stereochemistry upon the position of the ν(CO) band, it can be concluded that strong π-acceptors, such as COPh or $SnCl_3$, shift the band further towards higher energies (approx. 100 cm^{-1}), relative to the parent complex, than do weak π-acceptors, such as methyl or allyl (approx. 80 cm^{-1}).

Experimental

Analyses were carried out with a Perkin-Elmer 240 C, H and N microanalyzer. IR spectra were recorded (in the range 4000—200 cm^{-1}) on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene disks or in solution between NaCl disks. Molecular weights were measured with a Perkin-Elmer 115 osmometer and melting points were determined with a Buchi apparatus (Dr. Tottoli model) and with a Reichert-Kofler hot-stage microscope using silicone suspensions of the solids. ^{1}H NMR spectra were recorded on a Varian EM-390 90 MHz spectrophotometer. Conductivities were measured in ca. 5×10^{-4} M acetone solution.

All the reactions were carried out in conventional flasks under dry argon. The solvents were distilled and deoxygenated before use. $[Ir(\mu\text{-}Cl)(COD)]_2$ was prepared as described elsewhere [21]. The other reagents were commercially obtained. The reactions were carried out at room temperature.

Preparation of [Ir(Oq)(COD)] (I)

2 mmol of sodium hydroxide in 2 ml of water were added to a solution of 8-hydroxyquinoline (0.145 g, 1 mmol) in 10 ml of methanol. After addition of 0.332 g (0.5 mmol) of $[Ir(\mu\text{-}Cl)(COD)]_2$ and 15 min stirring, the dark red precipitate was filtered off, washed thoroughly with water followed by 3 × 2 ml of cold methanol and then air-dried. (Yield: 0.410 g, 90%). ^{1}H NMR spectrum (in $CDCl_3$ solution) τ, 1.68 (d, 1H); 1.90 (d, 1H); 2.57 (m, 2H); 2.90 (m, 2H); 5.35 (m, 2H); 6.20 (m, 2H); 7.60 (m, 4H); 8.18 (m, 4H).

Preparation of [Ir(Oq)(CO)₂] (II)

Bubbling of CO for 30 min through a solution of [Ir(Oq)(COD)] (0.080 g, 0.18 mmol) in 10 ml of dichloromethane gave black crystals, which were filtered off, washed with diethyl ether, and vacuum-dried. (Yield: 0.050 g, 70%).

Preparation of [Ir(Oq)(COD)(PPh₃)] (V)

Addition of 0.18 g (0.4 mmol) of [Ir(Oq)(COD)] to a solution of 0.105 g (0.4 mmol) of PPh_3 in 15 ml of diethyl ether gave an orange-coloured solution, this was vacuum-concentrated to 5 ml, and the resulting crystals were filtered off, washed with pentane, and vacuum-dried. (Yield: 0.260 g, 88%).

Preparation of [Ir(Oq)(COD) {P(OPh)₃}] (VI)

Addition of 0.044 g (0.1 mmol) of [Ir(Oq)(COD)] to an excess of triphenyl-phosphite (0.04 ml) in ether gave an orange-coloured solution which was filtered through kieselguhr and vacuum-evaporated. The resulting oil was suspended in pentane, and the crystals obtained on scratching the walls were filtered off, washed with ether, and vacuum-dried. (Yield: 0.062 g, 82%). [Ir(Oq)(COD)(maleic anhydride)] (III) and [Ir (Oq)(COD) (TCNE)] (IV) were prepared by the above-described procedure.

Preparation of [Ir(Oq)(dppe)] (VII)

0.044 g (0.1 mmol) of [Ir(Oq)(COD)] was added to a solution of 0.040 g (0.1 mmol) of 1,2-bis(diphenylphosphino)ethane (dppe) in a mixture of 10 ml of ether and 5 ml of dichloromethane. Filtration through kieselguhr and vacuum evaporation rendered an orange-coloured oil which was dissolved in ca. 0.3 ml of dichloromethane, and then ether was added. The resulting crystals were filtered off, washed with ether and vacuum-dried.(Yield: 0.051 g, 63%).

Preparation of [Ir(Oq)(dppen)] (VIII)

0.044 g (0.1 mmol) of [Ir(Oq)(COD)] was added to a solution of 0.080 g (0.2 mmol) of *cis*-1,2-bis(diphenylphosphino)ethylene (dppen) in 10 ml of ether. The solution was vacuum-evaporated and the residue was treated with dichloromethane-ether. The formed crystals were filtered off, washed with ether, and vacuum-dried. (Yield: 0.075 g, 89%).

Preparation of [Ir(Oq)(CO)PPh₃] (IX)

CO was bubbled for 15 min through a solution of 0.058 g (0.082 mmol) of [Ir(Oq)(COD)PPh₃] in 10 ml of dichloromethane, and the solution was then vacuum-evaporated to ca. 1 ml, to give red crystals. The crystallization was completed by addition of ether. The complex was filtered off, washed with ether, and vacuum-dried. (Yield: 0.030 g, 60%). ¹H NMR spectrum (in CDCl₃ solution), τ, 0.88 (t, 1H); 1.65 (d, 1H); 2.20 (m, 6H); 2.58 (m, 10H); 2.98 (d, 2H); 3.06 (d, 1H).

Preparation of [Ir(Oq)(CO) {P(OPh)₃}] (X)

0.06 ml of triphenylphosphite was added to a suspension of 0.058 g, (0.15 mmol) of [Ir(Oq)(CO)₂] in 10 ml of ether and stirred for 1 h. The yellow solid formed was filtered off, washed with ether, and vacuum-dried. (Yield: 0.080 g, 80%).

The reactions of carbon monoxide with [Ir(Oq)(COD) {P(OPh)₃}], [Ir(Oq)-(COD)(maleic anhydride)] and [Ir(Oq)(COD)(TCNE)] to give X and II were carried out by the above procedure and monitored by IR spectroscopy.

Preparation of complexes of the [Ir(Oq)(CO)(PR₃)] type

[Ir(Oq)(CO) {P(4-MeOPh)₃}] (XI). 0.335 g (0.5 mmol) of [Ir(μ-Cl)(COD)]₂ was added to a solution of sodium 8-oxyquinolate (0.167 g, 1 mmol) in a mixture of 50 ml of tetrahydrofuran and 10 ml of water. After 10 min, tris(4-methoxyphenyl)-phosphine (0.352 g, 1 mmol) was dissolved in the red solution, and CO was subsequently bubbled through the mixture for 30 min.

Vacuum evaporation gave an oily residue, which was washed with water and cold methanol (2 × 2 ml) and finally extracted with 20 ml of dichloromethane. The extract was dried with magnesium sulfate, then evaporated to give an orange oil, which was crystallized by addition of ether. The crystals were filtered off, washed with a small amount of ether, and vacuum-dried. (Yield: 0.60 g, 85%).

[Ir(Oq)(CO)(PPh$_3$)] (IX) was measured similarly

[Ir(Oq)(CO){P(4-MePh)$_3$}] (XII) and [Ir(Oq)(CO){P(4-ClPh)$_3$}] (XIII). These were prepared as described above, though the oily residue was washed only with water (not with methanol) and the orange-coloured oil was precipitated with hexane.

Oxidative addition reactions
These reactions were carried out under identical conditions and examples of each type are described below for complex IX as starting material.

a) Reaction with benzoyl chloride. 0.05 ml of benzoyl chloride was added to 0.063 g (0.1 mmol) of complex IX in 10 ml of dichloromethane. The solution was vacuum-evaporated and the residue was stirred for 15 min with 4 ml of ether. The resulting complex (XIV) was filtered off, washed thoroughly with hexane, and air-dried. (Yield: 0.072 g, 95%).

b) With acetyl chloride. Addition of an excess of acetyl chloride (0.05 ml) to a solution of 0.063 g (0.1 mmol) of [Ir(Oq)(CO)(PPh$_3$)] (complex IX) in 10 ml of dichloromethane caused the orange-coloured solution to turn yellow. Vacuum-evaporation gave a residue, which was dissolved in 0.5 ml of dichloromethane and precipitated by addition of ether. The resulting complex (XV) was filtered off, washed with hexane, and vacuum-dried. (Yield: 0.059 g, 85%).

c) Reaction with methyl-iodide. 0.1 ml of methyl-iodide was added dropwise to 0.0509 g (0.08 mmol) of complex IX in 10 ml of dichloromethane. Vacuum-evaporation and treatment of the residue with dichloromethane-ether gave crystals of complex XIX, which were filtered off, washed with hexane and vacuum-dried. (Yield: 0.040 g, 65%).

d) Reaction with allyl-bromide. 0.05 ml of allyl-bromide were added to 0.080 g (0.13 mmol) of complex IX in 10 ml of dichloromethane. Vacuum-evaporation gave a solid which was recrystallized from dichloromethane-ether to give complex XXIII, which was washed with hexane, and air-dried. (Yield: 0.080 g, 82%).

e) Reaction with tin tetrachloride. 0.05 ml of anhydrous tin tetrachloride was added dropwise to 0.063 g (0.1 mmol) of complex IX in 10 ml of dichloromethane, the solution was vacuum-evaporated, and the residue was crystallized from dichloromethane-hexane. Complex XXVII was filtered off, washed with hexane and vacuum-dried. (Yield: 0.0853 g, 96%).

f) Reaction with chlorotrimethyltin. 0.020 g (0.1 mmol) of chlorotrimethyltin was treated for 45 min with 0.063 g (0.1 mmol) of complex IX in 10 ml of dichloromethane, without exclusion of air. Vacuum-evaporation and treatment of the residue with dichloromethane-hexane gave complex XXXI which was filtered off, washed with hexane and vacuum-dried. (Yield ~40%).

g) Reaction with chlorotrimethylsilane. 0.05 ml of chlorotrimethylsilane was

added dropwise to 0.063 g (0.1 mmol) of complex IX in 10 ml of dichloromethane. The solution was vacuum-evaporated and the residue was recrystallized from dichloromethane-ether. The obtained complex XXXIII was filtered off, washed with hexane and vacuum-dried. (Yield: 0.050 g, 70%).

h) Reaction with chlorine. Dry chlorine was slowly bubbled for 1 h through a dichloromethane solution of $[Ir(Oq)(CO)PPh_3)]$ (0.063 g, 0.1 mmol). Evaporation to dryness and treatment with dichloromethane-ether gave white crystals of complex XXXVII, which were washed with ether and air-dried. (Yield: 0.047 g, 52%).

i) Reaction with thallium trichloride. Solid thallium trichloride (0.031 g, 0.1 mmol) was added to a solution of complex IX (0.063 g, 0.1 mmol) in 20 ml of dichloromethane. After 15 min a second portion of thallium trichloride (0.010 g, 0.03 mmol) was added, and the mixture was stirred for 24 h at room temperature. Filtration through kieselguhr and evaporation of the filtrate to dryness gave a residue which was treated with dichloromethane-ether to yield dark-yellow crystals of the *trans* complex XXXVIII, which was filtered off, washed with ether and air-dried. (Yield: 0.030 g, 41%).

The filtrate and the washing liquids were combined evaporated in vacuo and the resulting residue was partially dissolved in ether. Addition of hexane caused precipitation of a yellow compound (mixture of the *cis* and *trans* isomers), which was filtered off, washed with hexane and air-dried. (Yield: 0.012 g, 16%).

j) Reaction with bromine. (0.1 mmol) of bromine in dichloromethane was treated with an equimolecular amount of complex IX in the same solvent. The solution was vacuum-evaporated and the residue was treated with 1 ml of dichloromethane. Addition of hexane gave complex XXXIX, which was filtered off, washed with hexane and air-dried. (Yield: 0.063 g, ~70%).

k) Reaction with hydrogen chloride. A dry hydrogen chloride stream was bubbled for 1 min through a solution of complex IX (0.063 g, 0.1 mmol) in 10 ml of dichloromethane. The resulting pale yellow solution was evaporated to dryness, and the residue was recrystallized from dichloromethane-ether to give a cream-coloured solid, which was washed with ether and air-dried to give $[IrHCl(Oq)(CO)(PPh_3)]$. (Yield: 0.054 g, 82%).

Acknowledgements

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