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An iridium-193 and gold-197 Mössbauer investigation of iridium(I), iridium(III) and iridium(I)/gold(I) complexes

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Abstract

Comparison of the ^{193}Ir and ^{197}Au Mössbauer spectra of the series *trans*-$(Ph_3P)_2Ir(CO)X$, *trans,cis*-$(Ph_3P)_2(H)_2Ir(CO)(X)$ (X = Cl or pz-*N*; pzH = 3,5-dimethyl-, 3,5-dimethyl-4-nitro-, 3,5-bis(trifluoromethyl)pyrazole) and *trans*-$(Ph_3P)_2(CO)Ir[\mu$-(3,5-dimethylpyrazolato-*N*,*N*′)]AuX′ (X′ = Cl, Br) shows that even the substituents on the heterocycle influence the electron density at the iridium nucleus and that the bridging pyrazolato ligand transmits electronic effects from gold to iridium through three bonds. The Mössbauer parameters are sensitive to the ligand X but not to the presence of conformers.

Introduction

Although the discovery of recoilless gamma resonance spectroscopy involved the 129 keV transition of ^{191}Ir nucleus [1] and even though the 73 keV transition in ^{193}Ir is reasonably suitable, Mössbauer studies of systems containing this element are rather scarce, probably because of experimental difficulties. Nevertheless, the general picture, as shown by reviews [2a], is clear enough to provide chemically useful information even though for several $(Ph_3P)_2Ir(CO)X$ complexes the Mössbauer parameters were found to be fairly insensitive to variation of X [3]. In continuation of our interest in this technique [4], we decided to apply both ^{193}Ir and ^{197}Au Mössbauer spectroscopy to a homogeneous series of well-characterized pyrazole derivatives containing either iridium alone [5a] or iridium and gold [5b]. In the first

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case the oxidation state is either +1 or +3, the difference being due to oxidative addition of dihydrogen, in the latter case Ir^I and Au^I. The stable bimetallic pyrazolato-bridged compounds investigated here recall the ligand-bridged intermediates postulated in the inner sphere reaction mechanism, for example the ion $[(H_2O)_5Cr{-}X{-}Co(NH_3)_5]^{4+}$ assumed to be present during reduction of $[Co(NH_3)_5X]^{2+}$ by aqueous chromium(II) [6].

Results and discussion

The spectral parameters IS, QS, and LW (isomer shift, quadrupole splitting, and linewidth in mm s^{-1}) are reported in Table. 1. All the ^{193}Ir spectra show only one quadrupole doublet, as shown in Fig. 1 for the iridium(III) derivative $(Ph_3P)_2(H)_2Ir(CO)[(3,5\text{-}CF_3)_2$pyrazolato-*N*] (**9**). The ^{197}Au spectra of **5** and **6** show a single resolved quadrupole doublet. The linewidths are close to the minimum value (0.60 or 1.88 mm s^{-1} for ^{193}Ir or ^{197}Au, respectively), in agreement with the presence of only one type of distinguishable metal site.

Iridium(I) spectra

All the iridium(I) derivatives investigated here, **1**–**6**, are likely to have a square planar arrangement of the ligands around the metal, as shown by an X-ray crystal structure carried out on **4** [5a] and by the combined data collected for the other compounds by infrared and proton, carbon, phosphorus, or fluorine NMR spectroscopy [5]. However, such coordination, though likely, cannot be proved beyond doubt in the solid state: indeed, most of the spectra are recorded in solution and the X-ray crystal structure gives information only on the solid state form which crystallizes out of the solution, and, finally, metal–metal interaction may lead to molecular stacking and to a coordination number higher than four. The existence of other forms was proved by infrared spectroscopy [5]; the possibility of a coordina-

Table 1

^{193}Ir and ^{197}Au Mössbauer parameters at 4.2 K

No.	X in compound	IS [a,b]	QS [a]	LW [a]
trans-$(Ph_3P)_2Ir(CO)X$:				
1	Cl	0.05(2)	7.74(3)	0.75(3)
2	3,5-Me_2pz-*N*	−0.38(1)	8.41(2)	0.72(4)
3	3,5-Me_2-4-NO_2pz-*N*	−0.37(1) [c]	8.30(2)	0.70(2)
4	3,5-$(CF_3)_2$pz-*N*	−0.43(1)	7.93(2)	0.76(4)
5	[μ-(3,5-Me_2pz-*N*,*N′*)]AuCl	−0.50(1)	7.22(2)	0.64(3)
	idem, gold spectrum	1.02(1) [d]	6.43(2)	1.97(3)
6	[μ-(3,5-Me_2pz-*N*,*N′*)]AuBr	−0.49(2)	7.45(4)	0.77(9)
	idem, gold spectrum	0.98(3) [d]	6.58(4)	1.98(9)
trans,cis-$(Ph_3P)_2(H)_2Ir(CO)X$:				
7	3,5-Me_2pz-*N*	−0.19(1)	3.20(1)	0.66(2)
8	3,5-Me_2-4-NO_2pz-*N*	−0.17(1)	3.16(2)	0.64(3)
9	3.5-$(CF_3)_2$pz-*N*	−0.25(2)	3.62(1)	0.65(2)

[a] IS, QS, and LW are isomer, shift, quadrupole splitting, and linewidth in mm s^{-1}. [b] Ref. to Ir metal. [c] An additional quadrupole doublet [IS −0.86(4), QS 1.33(6), LS 0.68(3)] is probably due to partial decomposition of the sample during storage. [d] Ref. to Pt/Au source.

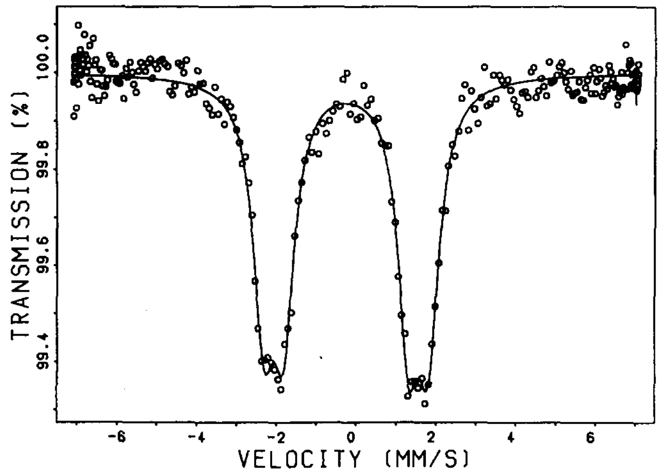

Fig. 1. ^{193}Ir spectrum of the iridium(III) derivative *trans,cis*-$(Ph_3P)_2(H)_2Ir(CO)[(3,5\text{-}CF_3)_2$-pyrazolato-*N*] (9).

tion number higher than four can now also be excluded for the solid state. The combined values of IS and QS are, in fact, compatible only with a square-planar arrangement of the ligand and rule out stacking, which is generally accompanied by a large decrease in QS (1 mm s^{-1} [2b]). In addition, the square-planar coordination is maintained in each of the forms of the compounds **2**, **3**, or **4**: the samples do indeed contain different forms, each characterized by its infrared CO stretching frequency. There must be only one metal site in **2–4** and the solid state differences can be explained in terms of different orientation of the bulky ligands around the metal as suggested by the structural data for our and for related compounds [5]. Although the parameters of iridium(III) (see below) are sensitive to the ligands surrounding the metal, they do not reveal the presence of conformers, which are detected by other techniques: a similar conclusion was previously reached in the case of ^{197}Au spectroscopy [4b] when geometric isomers were examined.

The values of IS and especially of QS for the Ir^I derivatives **1–6** lie in a rather restricted range (0.5 and 1.2 mm s^{-1}, respectively). As with other square-planar Ir^I compounds, there are likely to be only small differences in the electronic environment of the iridium nuclei because of the so-called "compensation effect" [3b]. The IS values alone are not sufficient to prove that the oxidation number is +1, since the values for Ir^{III} derivatives also fall in a similar range, but fortunately the QS values are significantly bigger for Ir^I than for Ir^{III} compounds.l

For the iridium(I) complexes *trans*-$(Ph_3P)_2Ir(CO)X$ reported here the IS value becomes more negative along the series X = chloride (**1**), 3,5-dimethyl- (**2**) or 3,5-dimethyl-4-nitro- (**3**) and 3,5-bis(trifluoromethyl)-pyrazolato (**4**), in line with decreasing 6*s* orbital occupation and increasing acceptance from 5*d* orbitals. This view is supported by consideration of the QS values; these are proportional to the valence electron contribution to the electric field gradient (e.f.g.) around iridium, indicating that a variation in the occupation of the $5d_{(x^2-y^2)}$ orbitals takes place. For the complexes *trans*-$(Ph_3P)_2Ir(CO)X$ (X = Cl, Br, I, azide, SCN) [3b] the QS values are amongst the largest reported for Ir^I derivatives; they are even larger when

X is a pyrazole derivative (**2**–**4**), showing that there is a big, asymmetric e.f.g., i.e. a decrease in the $5d_{(x^2-y^2)}$ occupation. The shift of the IS and QS values on going from **2** to its AuCl (**5**) or AuBr (**6**) adducts corresponds to a decrease in the $6s$ electron population and an increase in the $5d$-electron density.

Although modest in size, the variations of IS and of QS with changes in the substituents on pyrazole show that these substituents influence the electron density around iridium. In cases **5** or **6** in particular, where one substituent is gold or, in other words, the pyrazolato ligand bridges gold and iridium atoms, comparison of their IS and QS values with those of **2** suggests that the ring transmits electron density from one metal to the other. On the other hand the gold atom transmits only a negligible amount of electronic density, since the ^{193}Ir IS values of the compounds **5** and **6** are unaffected by the change of the substituent on gold (chlorine or bromine, respectively); in addition, the QS values are nearly the same.

We should point out that other ligand-bridged systems have been extensively studied in order to gain insight into the mechanism of redox reactions [6]. Electron density transfer does take place in the Taube-type reactions and the intermediate has been studied almost exclusively by kinetic methods; compounds **5** and **6** provide possible means of looking at the ground state of ligand-bridged metal ions. The possibility of such an intramolecular electron transfer via the pyrazolato bridge accounts for our failure to characterize completely Au^{III}/Ir^{I} complexes having the same ligands, e.g. *trans*-$(Ph_3P)_2(CO)Ir(\mu$-pyrazolato$)AuCl_3$. Indeed, if significant electron transfer between Au^{I} and Ir^{I} is already operative in the ground state, it should surely much easier when on one side of the bridging ligand Au^{I} is replaced by a better acceptor such as Au^{III}. The latter has two electrons less than the former, so that the intramolecular redox reaction is likely to takes place very easily in *trans*-$(Ph_3P)_2(CO)Ir(\mu$-pyrazolato$)AuCl_3$: this molecule is indeed so unstable that it could be only partially characterized because it gives Ir^{III} and Au^{I}, which were isolated as $(Ph_3P)_2(CO)IrCl_3$ and gold(I) pyrazolate, respectively [5a].

Iridium(III) spectra

The combined spectroscopic evidence indicates that compounds **7**–**9** are analogous to the species [*trans,cis*-$(Ph_3P)_2(H)_2Ir(CO)($pyrazole-*N*$)]BF_4 \cdot$ 2toluene or *trans,cis*-$(Ph_3P)_2(H)_2Ir(CO)(\mu$-pyrazolate-*N*,*N*′$)AuCl$ for which X-ray crystal structures are available, and so they are likely to contain octahedrally coordinated iridium(III) [5a]. This coordination is supported by their low QS values (3.1–3.6 mm s^{-1}); these are consistent with the absence of the valence contribution and arise only from the lattice contribution to the e.f.g. Inside the series the IS values reflect the strength of donation to the iridium $6s$ orbitals: 3,5-$(CF_3)_2$pz < 3,5-Me_2Pz $\leqslant$ 3,5-Me_2-4-NO_2pz; the IS values are less negative than for the Ir^{I} compounds. Only one ^{193}Ir doublet is found, and its width approaches the natural value, so that there must be only one metal site in **7**–**9**.

An attempt was made to simulate the Mössbauer data of the iridium(III) complexes listed in Table 1 by the additive model, extensively used in low-spin iron(II) chemistry. No correlation was obtained, probably for one or more of the following reasons: large geometrical distortion in the pyrazolato derivatives, the diffuse character of the iridium $5d$ orbitals, and delocalization of the coordinate bonds.

Gold(I) spectra

The IS and QS values found for **5** lie in the range typical for the several compounds having an N–Au^I–Cl arrangement of ligands [4c]. This type of coordination for both **5** and **6** is also suggested by the agreement between experimental and calculated QS values assuming *sp* hybridization. According to the additive model, the resulting QS are 6.72 and 6.76 mm s^{-1} for **5** and **6** if 1.54, 1.56 and 1.83 mm s^{-1} are taken as partial quadrupole splitting for chloride, bromide, and the heterocycle, while 6.43(2) and 6.85(4) mm s^{-1}, respectively, are the experimental values.

Experimental

The samples were made by published methods [5] and their identities checked by C,H,N microanalyses and infrared and NMR spectroscopy.

In the iridium spectra the ^{193}Os activity feeding the 73 keV Mössbauer transition was produced by neutron irradiation of metallic osmium. Due to the hexagonal structure of the metal the source emits a quadrupole split line doublet with a separation of 0.48(2) mm s^{-1}; this was taken into account during the fitting procedure. In the gold spectra the ^{197}Pt activity feeding the 77.3 keV Mössbauer transition was produced by irradiation of enriched ^{196}Pt metal. Depending upon the compound, a sample of the absorber with a ^{197}Au of ca. 50 mg cm^{-2} was used. In both types of spectra both source and absorber were kept at 4.2 K, a sinusoidal velocity waveform and an intrinsic Ge detector were used. The reported shifts are relative to iridium metal or to Pt/Au source for ^{193}Ir or ^{197}Au spectra, respectively.

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