Preliminary Communication

The unexpected formal insertion of a carbonyl group into a heterocyclic *N–Ir* bond

Miguel A. Ciriano [a], Maurizio Lanfranchi [b], Luis A. Oro [a], Jesús J. Pérez-Torrente [a], Antonio Tiripicchio [b] and Marisa Tiripicchio Camellini [b]

[a] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Consejo Superior de Investigaciones Cientificas-Universidad de Zaragoza, E-50009 Zaragoza (Spain)*

[b] *Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Università di Parma, Viale delle Scienze 78, I-43100 Parma (Italy)*

(Received October 15, 1993)

Abstract

Reaction of the dioxygen complex $[Ir(C_7H_4NS_2)(O_2)(CO)(PPh_3)_2]$ ($C_7H_4NS_2$ = benzothiazole-2-thiolate) with SO_2 produces the unprecedented incorporation of the carbonyl group into the benzothiazole-2-thiolate ligand through the heterocyclic nitrogen, in addition to the oxidation to sulfate, yielding $[\overline{Ir\{C(O)NC(S)}SC_6H_4\}(SO_4)(PPh_3)_2]$.

Key words: Iridium; X-ray diffraction; Carbonyl insertion; Phosphine; Dioxygen; Sulfur dioxide

Nucleophilic attack on a carbonyl ligand is a well-known way of activation of the otherwise inert carbon monoxide with wide implications for the homogeneous catalysis of the water gas shift and related reactions [1]. Typical nucleophiles are alkoxy and hydroxy derivatives, and primary and secondary amines. Tertiary amines and heterocyclic nitrogen compounds do not undergo this reaction due to their reluctance to give formyl derivatives.

We report here a reaction that involves the unprecedented attack of a heterocyclic nitrogen atom on coordinated carbon monoxide, resulting in a formal insertion of CO into the metal-nitrogen bond without loss of the aromaticity of the heterocyclic ring.

In the course of our studies on the reactivity of the complex $[Ir(C_7H_4NS_2)(CO)(PPh_3)_2]$ (**1**) ($C_7H_4NS_2$ = benzothiazole-2-thiolate) [2*], an analogue of the Vaska's complex, we have found that it reacts with dioxygen in tetrahydrofuran or dichloromethane solutions to give the dioxygen complex $[Ir(C_7H_4NS_2)(O_2)(CO)(PPh_3)_2]$ (**2**). This reaction is irreversible and quantitative under rigorously anhydrous conditions. Complex **2** is isolated from tetrahydrofuran–hexane mixtures as a yellow, highly water-sensitive solid, which shows a ν(O–O) band at 885 cm^{-1} characteristic of η^2-dioxygen or peroxocomplexes [3]. The shift of the ν(CO) from 1966 cm^{-1} in **1** to 2015(s) cm^{-1} (in CH_2Cl_2) in **2** indicates the formal oxidation of the metal in the reaction. Complex **2** is octahedral with two equivalent phosphines in axial positions and the dioxygen, the carbonyl and the benzothiazole-2-thiolate ligands in equatorial positions. As the η^2-dioxygen occupies two *cis* coordination sites, the benzothiazole-2-thiolate is bound to the iridium atom either through the nitrogen or the sulfur atom only (Scheme 1).

Reaction of **2** in tetrahydrofuran with SO_2 under atmospheric pressure gives the sulfato-complex **3** isolated as yellow crystals in 70% yield. Surprisingly, complex **3** does not have a terminal carbonyl, as its IR spectrum shows a ν(C=O) band at 1680 cm^{-1}; furthermore, the molecular ion in the mass spectrum corresponds to the formula $[Ir(C_7H_4NS_2)(SO_4)(CO)(PPh_3)_2]$. The X-ray diffraction study of **3** [4*] has revealed that an unusual insertion of the carbonyl group into the metal–nitrogen bond has taken place, as in recently reported studies on rhodum imido complexes [5].

In the crystals of **3** two crystallographically independent, but practically identical, $[\overline{Ir\{C(O)NC(S)}SC_6H_4\}(SO_4)(PPh_3)_2]$, complexes are present. The structure of one of them is shown in Fig. 1 together with the most significant bond distances and angles. In the octahedral coordination around the iridium atom the two axial positions are occupied by P atoms from PPh_3, whereas two *cis*-equatorial sites are occupied by O atoms from the chelating sulfate and the remaining two by a C atom and a sulfur atom from the new ligand, which has also preserved its planarity after insertion of the adjacent CO ligand. The rather long N–C(O) bond could be a consequence of partial positive charge on the nitrogen, as implied by the resonance structures of the

---

Correspondence to: Professor L.A. Oro or Professor A. Tiripicchio.

* Reference number with asterisk indicates a note in the list of references.

0022-328X/94/$7.00
SSDI 0022-328X(93)24354-8

new ligand (Scheme 2). In addition, this length may reflect a weak or incipient N–C bond, as suggested by the mass spectrum of 3 which shows the sequential loss of sulfate and then carbonyl from the molecular ion. Such a fragmentation of formamides with loss of the carbonyl group is not observed. The bonding should be similar to that observed in *N*-acylderivatives of pyridine, which are proposed to be intermediates in acylation reactions of organic substrates, where 4-dimethylaminopyridine is added to promote the reaction [6]. The *N*-acylderivative transfers the acyl group easily because of the instability associated with the weak N–C(O) bond.

The reaction described here probably involves two different steps (Scheme 1). The first involves the action of SO_2 as an electrophile on the dioxygen, which opens the dioxometallacycle and adds in a polar fashion to complex **2** as described in the reactions of dioxygen complexes with various substrates [7]. Consequently, the insertion of sulfur into the O–O bond generates the sulfato ligand. As the benzothiazole-2-thiolate still has one potential donor unbound, there are two different but indistinguishable possibilities for the second step, depending on whether S or N is bonded to the iridium atom. However, molecular models suggest that the *S*-coordination of the benzothiazole-2-thiolate is preferred for steric reasons. In this case, the free

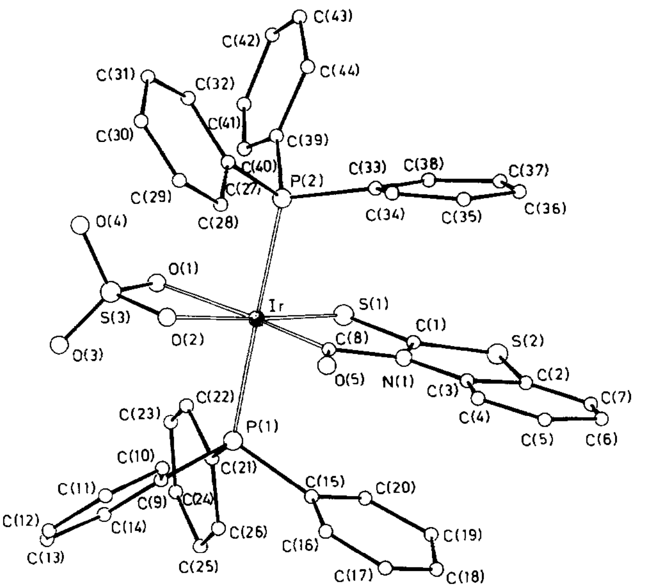
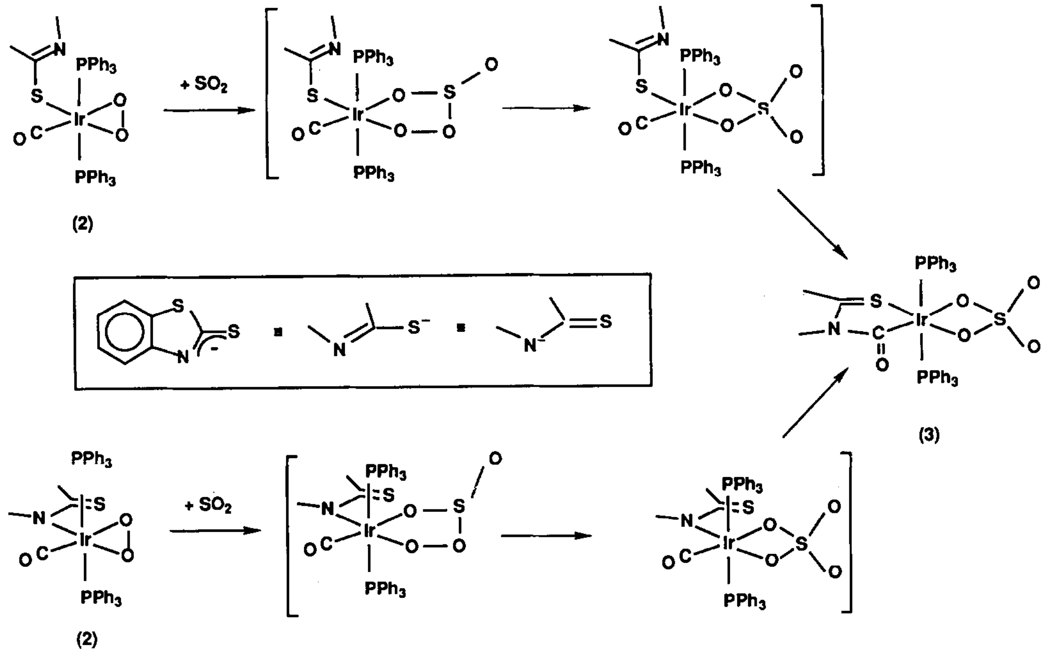
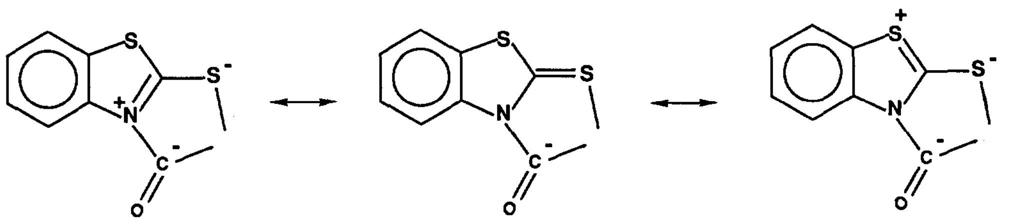


Fig. 1. View of the structure of 3. Selected bond distances (Å) and angles (°): Ir–P(1) 2.368(4) [2.376(4)], Ir–P(2) 2.386(5) [2.367(4)], Ir–O(1) 2.154(9) [2.187(9)], Ir–O(2) 2.067(8) [2.123(8)], Ir–C(8) 1.963(14) [1.926(12)], Ir–S(1) 2.322(4) [2.292(4)], C(8)–O(5) 1.195(18) [1.208(16)], N(1)–C(8) 1.509(20) [1.491(17)], N(1)–C(1) 1.332(18) [1.346(19)], C(1)–S(1) 1.707(14) [1.673(14)]; C(8)–Ir–S(1) 86.1(5) [87.3(4)], O(1)–Ir–O(2) 66.4(4) [65.2(4)], Ir–C(8)–O(5) 129.9(13) [130.2(11)]. The values in square brackets refer to the second independent molecule.



Scheme 1.



Scheme 2.

nitrogen simply adds to the carbonyl group to give the new organic ligand. An alternative would be that the carbonyl inserts into the N–Ir bond while the sulfur atom fills the vacant coordination position. Both possibilities have been proposed for reactions of carbon monoxide with amido- and imido-complexes of rhodium [5]. In any case, the final result is the carbonylation of the nitrogen in a heterocyclic ring to give a new organic ligand without loss of any aromaticity.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (DGICYT) (GRANT PB88-0056) and Consiglio Nazionale delle Ricerche (Rome) for financial support.

References

1 P.C. Ford and A. Rokicki, *Adv. Organomet. Chem.*, *28* (1988) 139.

2 *Selected spectroscopic properties for the new compounds.* **1**: $^{31}P\{^1H\}$ NMR (80.98 MHz, $CDCl_3$, H_3PO_4 85%): δ 26.6 (s). **2**: $^{31}P\{^1H\}$ NMR (80.98 MHz, $CDCl_3$, H_3PO_4 85%): δ 6.1 (s). **3**: $^{31}P\{^1H\}$ NMR (80.98 MHz, $CDCl_3$, H_3PO_4 85%): δ −5.9 (s); Mass spectrum (FAB): m/z 1007 (M^+, 47%), 911 ($M^+ - SO_4$, 28), 882 ($M^+ - SO_4 - CO$, 100); IR: ν_{max}/cm^{-1} 1257, 1155, 927, 890, 695, 650 (SO_4). All the new compounds gave correct elemental analyses.

3 H. Mimoun, *Comprehensive Coordination Chemistry*, Vol. 6, Pergamon Press, Oxford 1987, p. 317; M.H. Gubelmann and A.F. Williams, *Struc. Bonding (Berlin)*, *55* (1983) 1.

4 *Crystal data* for **3**: $C_{44}H_{34}IrNO_5P_2S_3$, $M = 1007.10$, monoclinic, space group $P2_1$, $a = 14.414(8)$, $b = 20.220(6)$, $c = 14.800(5)$ Å, $\beta = 107.41(2)°$, $V = 4116(3)$ Å^3, $Z = 4$, $D_c = 1.625$ g cm^{-3}, $F(000) = 2000$, nickel-filtered Cu-Kα radiation, $\lambda = 1.54178$ Å, $\mu = 86.92$ cm^{-1}.

The intensity data for the compounds were collected on a Siemens AED diffractometer, using the θ–2θ scan technique at room temperature. 8374 unique reflections were measured with θ in the range 3–70°; 5324, having $I > 2\sigma(I)$, were used in the refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures, with anisotropic thermal parameters in the last cycles of refinement for all non-hydrogen atoms, excepting the carbon atoms of the phenyl rings.

All hydrogen atoms were placed at their geometrically calculated positions and refined "riding" on the corresponding carbon atoms. The R and R_w values were 0.0423 and 0.0526. Because the space group $P2_1$ leads to a chiral configuration in the structure, an independant final cycle of refinement was carried out using the coordinates $-x$, $-y$, $-z$ for the non-hydrogen atoms. An improvement in R values was obtained [$R(x,y,z) = 0.046$; $R(-x,-y,-z) = 0.0449$]. The latter model was selected and the reported data refer to this model. Atomic co-ordinates, thermal parameters and a complete list of bond distances and angles have been deposited at Cambridge Crystallographic Data Centre.

5 Y.W. Ge and P.R. Sharp, *Organometallics*, *7* (1988) 2234; Y.W. Ge and P.R. Sharp, *Inorg. Chem.*, *31* (1992) 379.

6 E.F.V. Scriven, *Comprehensive Heterocyclic Chemistry*, Vol. 2, Pergamon Press, Oxford, 1984, Ch. 2.05, p. 180.

7 Y. Wakatsuki, M. Maniwa and H. Yamazaki, *Inorg. Chem.*, *29* (1990) 4204; H.J. Lawson and J.D. Atwood, *J. Am. Chem. Soc.*, *111* (1989) 6223; Y. Tatsuno and S. Otsuka, *J. Am. Chem. Soc.*, *103* (1981) 5832; W.B. Beaulieu, G.D. Mercer and D.M. Roundhill, *J. Am. Chem. Soc.*, *100* (1978) 1147.