Displacement of Coordinated Carbon Monoxide as a Result of an Intramolecular Nucleophilic Attack. Crystal and Molecular Structure of the 'Intermediate', *cis*-Dicarbonyl bis(pyridine-2-thiolato)triphenylphosphineruthenium(II), and of the Product, Monocarbonyl bis(pyridine-2-thiolato)triphenylphosphine ruthenium(II)

PASQUALE MURA*

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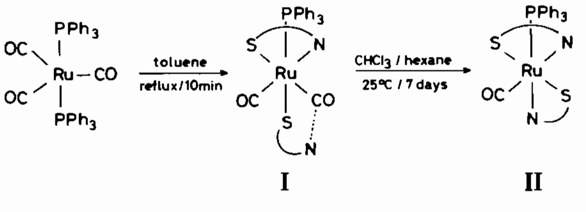
Coordination of carbon monoxide places a positive charge on the carbon atom and renders it susceptible to nucleophilic attack. This situation, which was first confirmed by the molecular orbital calculations of Caulton and Fenske [1], has been exploited in numerous synthetic reactions [2] leading to a wide variety of products including carbene [3], isocyanate [4], carboxamido [5], and alkoxycarbonyl [6] complexes of the transition metals. However, relatively little is known about the intermediates generated in the course of these reactions. We now report the crystal structures of two ruthenium complexes, [Ru(pyS)$_2$(CO)$_2$(PPh$_3$)] (I) and [Ru(pyS)$_2$(CO)(PPh$_3$)] (II) [pyS = o-SC$_5$H$_4$N], which appear to provide examples of an 'intermediate' and the product respectively in a nucleophilic attack on a coordinated carbonyl group.

The complex [Ru(CO)$_3$(PPh$_3$)$_2$] [7] reacts with 2,2′-dipyridyldisulphide (py S.S py) in boiling toluene under controlled conditions to afford the dicarbonyl (I). This latter compound subsequently loses a molecule of CO on standing for several days in chloroform/n-hexane solution at ambient temperature, to yield the monocarbonyl product (II).



Both complexes are air-stable yellow crystalline solids.

The molecular structure of [Ru(pyS)$_2$(CO)$_2$(PPh$_3$)] (I) is shown in Fig. 1; the most interesting feature being the steric juxtapositioning of the S-bonded pyridine-2-thiolate ligand and one of the carbonyl groups, which leads to a carbon–nitrogen distance N(2)–C(2) of 2.782(7) Å, *i.e. ca.* 0.5 Å less than the sum of the nitrogen and carbon Van der Waal's radii. This arrangement could conceivably reflect molecular packing interactions, or stereochemical constraints within the ruthenium coordination sphere. However, given the ease with which a carbonyl ligand is lost from (I) it seems probable that the short nitrogen–carbon distance is in fact indicative of an incipient nucleophilic attack on the carbon atom of the carbonyl group by the nitrogen atom of the monodentate pyridine-2-thiolate ligand. Flow of electron density from the nitrogen lone pair into the π^* anti-bonding orbital of the C–O multiple bond

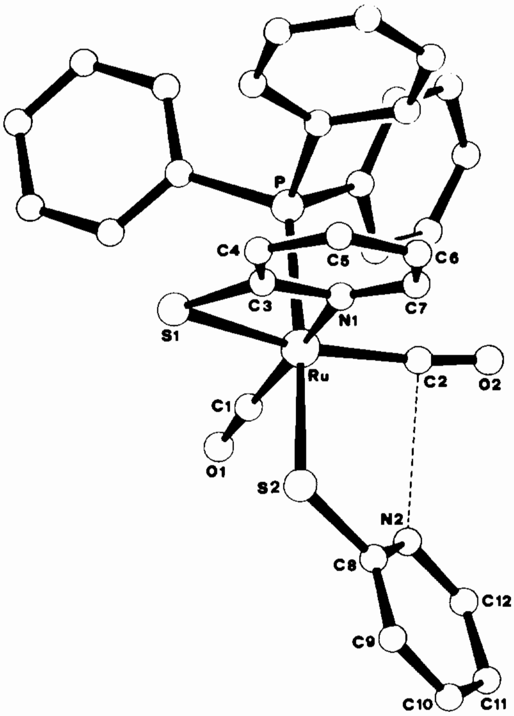


Fig. 1. I; non bonded distance N(2)···C(2) 2.782(7) Å. Some significant bond distances (Å) and angles (°) are: Ru–S(1) 2.453(1), Ru–S(2) 2.419(1), Ru–P 2.367(1), Ru–N(1) 2.114(4), Ru–C(1) 1.884(5) Ru–C(2) 1.895(5), C(1)–O(1) 1.133(6), C(2)–O(2) 1.124(4); S(1)–Ru–S(2) 85.5(1), S(1)–Ru–P 86.8(<1), S(1)–Ru–N(1) 67.6(1), S(1)–Ru–C(1) 103.9(2), S(1)–Ru–C(2) 161.4(2), S(2)–Ru–P 172.1(<1), S(2)–Ru–C(1) 88.2(2), S(2)–Ru–C(2) 94.7(2), P–Ru–N(1) 92.0(1), P–Ru–C(1) 95.6(2), P–Ru–C(2) 91.9(2), Ru–C(1)–O(1) 176.3(5), Ru–C(2)–O(2) 174.4(5), N(1)–Ru–C(1) 168.4(2).

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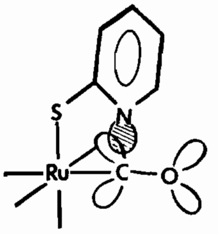
(Scheme 1) would serve to weaken the π-component of the ruthenium–carbonyl bond and thus facilitate loss of the carbonyl ligand. It has been pointed out that nucleophilic attack at carbon can be predicted on the basis of force constants [8] and in a less rigorous way, when force constants are not available, by considering the ν(CO) values [5]. It is significant that for $[Ru(pyS)_2(CO)_2(PPh_3)]$ the higher of the two ν(CO) values (2035 cm^{-1}) is near the threshold found for carbonyl ligands susceptible to nucleophilic attack [5].



Scheme 1

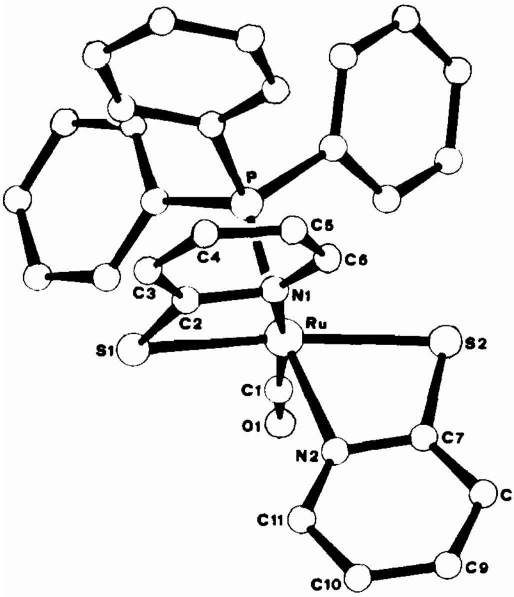


Fig. 2. **II**; some significant bond distances (Å) and angles (°) are: Ru–S(1) 2.429(1), Ru–S(2) 2.422(1), Ru–P 2.309(1), Ru–N(1) 2.138(2), Ru–N(2) 2.118(3), Ru–C(1) 1.844(3), C(1)–O(1) 1.146(4); S(1)–Ru–S(2) 157.96(3), S(1)–Ru–P 88.90(3), S(1)–Ru–N(1) 67.8(1), S(1)–Ru–N(2) 96.46(8), S(1)–Ru–C(1) 105.1(1), S(2)–Ru–P 105.22(3), S(2)–Ru–N(2) 67.51(9), S(2)–Ru–N(1) 94.2(1), S(2)–Ru–C(1) 91.7(1), P–Ru–N(2) 170.8(1), P–Ru–N(1) 92.75(7), P–Ru–C(1) 90.9(1), N(1)–Ru–C(1) 172.0(1), Ru–C(1)–O(1) 176.8(4).

The structure of the final product $[Ru(pyS)_2(CO)(PPh_3)]$ (**II**) is shown in Fig. 2. Loss of a carbonyl ligand and concomitant closing of the second chelate ring has clearly been accompanied by a rearrangement within the coordination sphere to give the thermodynamically preferred isomer. The stereochemistry, bond lengths and bond angles found for complex (**II**) are very similar to those previously reported [9] for the closely-related chelate $[Ru(pyS)_2(PPh_3)_2]$.

A full report on the synthesis and characterisation of these and other pyridine-2-thiolato complexes of the platinum group metals will be presented elsewhere [10].

References

1 K. G. Caulton and R. F. Fenske, *Inorg. Chem., 7,* 1273 (1968).
2 D. H. Gibson, K. Owens and T. S. Ong, *J. Am. Chem. Soc., 106,* 1125 (1984) and refs. therein.
3 E. O. Fisher, *Adv. Organomet. Chem., 14,* 1 (1976) and refs. therein.
4 H. Werner, W. Beck and H. Engelmann, *Inorg. Chim. Acta, 3,* 331 (1969).
5 R. J. Angelici and L. J. Blacik, *Inorg. Chem., 11,* 1754 (1972) and refs. therein.
6 R. J. Angelici, *Acc. Chem. Res., 5,* 335 (1972).
7 N. Ahmad, J. J. Levison, S. D. Robinson and M. F. Uttley, *Inorg. Synth., 15,* 50 (1974).
8 D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem., 9,* 1691 (1970).
9 S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.,* 635 (1972).
10 P. Mura, B. G. Olby and S. D. Robinson, in preparation.