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Preliminary communication

PREPARATION OF A NEW TYPE OF IMIDORUTHENIUM HYDRIDE COMPLEX

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Summary

Treatment of $RuH_2(PPh_3)_4$ with cyclic imides such as *d*-camphorimide, phthalimide, succinimide and methyl succinimide gave a new type of imidoruthenium hydride complex, $RuH(imido)(PPh_3)_3$, which has an imido ligand acting as bidentate ligand coordinated through its nitrogen and oxygen atoms.

It is well known that $RuH_2(PPh_3)_4$ (A) reacts with weakly acidic compounds, affording hydride complexes, $RuHX(PPh_3)_3$, where X is the conjugate base of a weak acid such as H_2O, CH_3NO_2, RCOOH [1]. However, reactions of this hydride complex with imides which have acidic hydrogens on nitrogen have not been reported. In reactions of A with cyclic anhydrides a ring cleavage reaction occurs [2], while no ring cleavage occurs with cyclic imides but rather a new type of imido complex was obtained. This communication deals with the preparation of such imido complexes and their properties.

Treatment of A with an imide (*d*-camphorimide, phthalimide, succinimide, methyl succinimide) gave imidoruthenium hydride complexes of the type $RuH(imido)(PPh_3)_3$ (I—IV), respectively. The structure of these complexes was confirmed by elemental analysis and IR and NMR spectra. Table 1 summarizes the analytical data for I—IV. For instance, reaction of *d*-camphorimide (0.26 g, 1.3 mmol) with an equimolar amount of A in toluene under argon at 60°C for 5 h gave an orange-yellow compound which was recrystallized from THF/hexane to yield yellow crystals of I in 65—80% yield. These complexes in the solid state are stable in the absence of air, but in solution extremely air-sensitive. The IR spectrum of each complex shows two strong bands at ca. 1700 and ca. 1550 cm^{-1}. These can be assigned to the carbonyl group of the imido ligand, the low frequency band being assigned to the carbonyl group coordinated to metal and the high frequency band being assigned to the free carbonyl group. (The free imide shows two bands in the 1700—1800 cm^{-1} range.) The position of a stretching

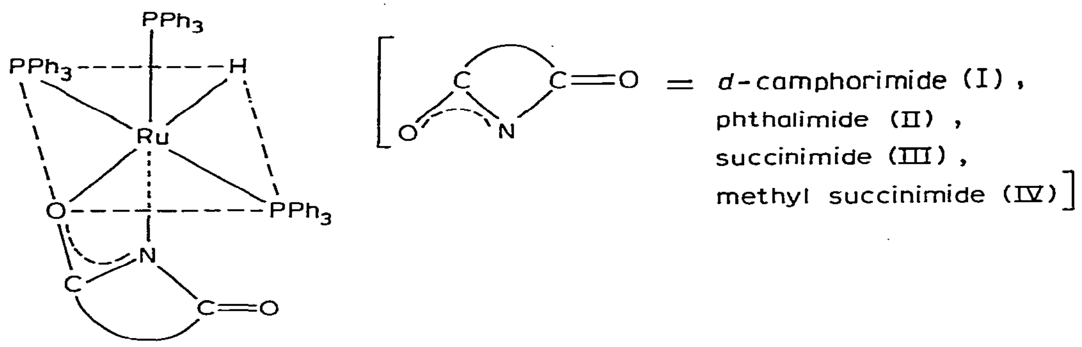

Fig. 1. Proposed structure for imidoruthenium hydride complexes I—IV.

band of the carbonyl group coordinated to the metal thus is shifted to lower frequency by about 150 cm^{-1} from its position in the free imide spectrum. In addition to the bands due to the carbonyl groups and phosphine ligands, the IR spectra of I—IV show a band due to the presence of the Ru—H group at 1900—2000 cm^{-1}, but no band due to the N—H group. This suggests that these complexes have the structure shown in Fig. 1.

The proposed structure of these complexes is further confirmed by their ^{1}H, ^{31}P and ^{13}C NMR spectra. The hydride proton appears at δ -16.5 to -17.6 ppm as a quartet due to ^{31}P coupling. This indicates that the three phosphine ligands are bonded to the metal in positions mutually *cis* to the hydride. The chemical shift of the hydride in these complexes is close to that observed in most other hydridoruthenium complexes which have the hydride *trans* to an O atom [1—3]. This suggests that the O atom of the imido group is *trans* to the hydride.

The ^{31}P{^{1}H}NMR spectrum of II shows a doublet (51.5 ppm downfield from external PPh$_3$) and a triplet (83.1 ppm) in 2/1 integrated intensity ratio, which is clearly characteristic of an AB$_2$ spin system, indicating that the three phosphine ligands are meridionally oriented. In contrast to that of II, the spectrum of I shows a doublet-of-doublets at 44.4 and 55.3 ppm and a less intense triplet at 79.4 ppm in 2/1 ratio (^{3}J(P—P)$_{trans}$ 294—295 Hz, ^{3}J(P—P)$_{cis}$ 28—33 Hz). This spectrum is characteristic of an ABX spin system, suggesting that the three phos-

TABLE 1

SPECTRAL AND ANALYTICAL DATA OF COMPOUNDS I—IV

Complex	Color	Yield (%)	M.p. (°C)	Analysis (%) Found (calcd.)			NMR^{a} (ppm)	IR^{b} (cm^{-1})		
				C	H	N	δ(Ru—H)	ν(Ru—H)	ν(C=O)	ν(C=O)
I	Pale yellow	80	218—219	72.1 (71.8)	5.5 (5.6)	1.3 (1.4)	-17.3	1995	1650	1510
II	Yellow	85	202—204	72.0 (71.9)	4.9 (4.8)	1.4 (1.4)	-16.5	1980	1710	1560
III	Pale yellow	75	214—216	70.5 (70.5)	5.1 (5.1)	1.3 (1.4)	-17.6	1975	1695	1540
IV	Pale yellow	65	223—225	70.2 (70.8)	5.3 (5.3)	1.4 (1.4)	-16.6 -17.4	1970	1710	1550

[a] In C$_6$D$_6$, TMS standard. [b] KBr tablet.

phine ligands in I are non-equivalent owing to the coordination of an optically active imide to ruthenium.

The ^{13}C NMR spectrum of I shows, in addition to resonances due to the aliphatic carbons of *d*-camphorimide, a singlet due to the carbonyl atom coordinated to ruthenium at δ(C) 193 ppm, and another singlet due to the free carbonyl carbon at δ(C) 185 ppm downfield from TMS. The free imide shows two carbonyl carbon resonances at δ(C) 176.4 and δ(C) 178.4 ppm.

These results indicate that I—IV have an imido ligand acting as a "bidentate ligand" with coordination through its nitrogen and oxygen atoms as shown in Fig. 1. To our knowledge this type of complex is the first example of an imido group bonded as a bidentate ligand [4]. Further studies on some reactions of I–IV, including the catalytic homogeneous hydrogenation of olefins and an X-ray structure analysis are in progress.

References

1 D.J. Cole-Hamilton and G. Wilkinson, Nouv. J. Chim., 1 (1977) 141.
2 T. Ikariya, K. Osakada and S. Yoshikawa, Tetrahedron Lett., (1978) 3749.
3 D. Rose, J.D. Gilbert, R.P. Robinson and G. Wilkinson, J. Chem. Soc. A, 9 (1969) 2610.
4 (a) D.M. Roundhill, Inorg. Chem., 9 (1970) 254;
(b) S.C. Jain and R. Rivert, J. Inorg. Nucl. Chem., 31 (1969) 399;
(c) T. Kohara, T. Yamamoto and A. Yamamoto, J. Organometal. Chem., 154 (1978) C37.