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ASYMMETRIC BENZENE—CHROMIUM(0) COMPLEXES HAVING THE METAL ATOM AS THE CHIRAL CENTER

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Summary

The first neutral chiral benzene—chromium(0) complexes of the type ArCr(CO)LL′ are described [1], where L is a phosphite and L′ an *N*-substituted maleimide. The vinylic protons are diastereotopic, and display a temperature-dependent NMR spectrum.

Results and discussion

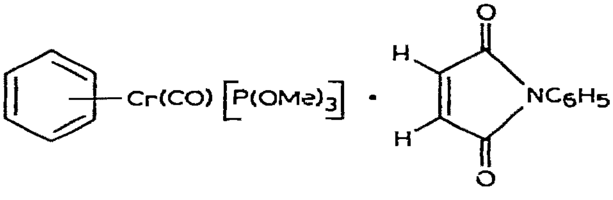
Several asymmetric organometallic complexes of the type CpM(CO)LL′ are known [2-6] in which the metal is the chiral center; some of them have been resolved into their enantiomers, the properties of which have been examined [7]. The only previously known asymmetric arene—chromium complex is the cation $C_6Me_6Cr(CO)(PPh_3)(NO)^+$ [8] and we now describe a similar neutral complex.

Our first attempts in the field were unsuccessful; all combinations of the usual *n* or *π* ligands of organo—transition metal chemistry such as phosphines, phosphites, dimethylsulphoxide, maleic anhydride [9], etc. yielded only very unstable, air-sensitive compounds. We have found, however, that the combination of the three ligands CO, $P(OR)_3$ and a maleimide [10] gives compounds which are reasonably stable and amenable to NMR study.

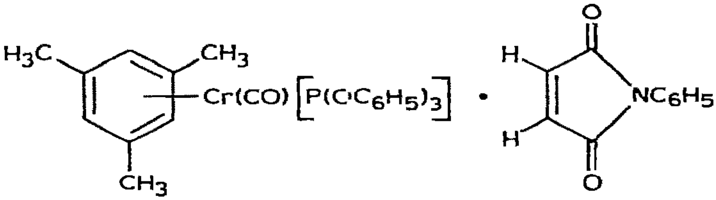
The photosubstitution of a carbonyl group of $ArCr(CO)_3$ by a maleimide (MI) yields the corresponding $ArCr(CO)_2(MI)$ with fair to good chemical yields (30-80%) and a high quantum yield [10]. When the resulting complex is irradiated in the presence of a phosphite, a second CO is replaced by the new ligand. Similar results are obtained by irradiating an $ArCr(CO)_2[P(OR)_3]$ complex together with the maleimide, and also, surprisingly, by photolyzing the parent arenechromium tricarbonyl in the presence of both L and L′. The irradiations were run in vacuum-degassed benzene solutions, and additional degassing at regular intervals removed the carbon monoxide but even so the yields of asymmetric complexes are very low (5-7%).

The structure of complexes I and II is based on the presence of only one metal-bonded carbonyl stretching band in the infrared, and on the general features of the NMR spectra, which also show that the olefinic protons of the maleimide ligand are diastereotopic.

For complex I, strong IR bands (CS_2) are found at 1881 cm^{-1} (MCO) and at 1730 and 1680 cm^{-1} (maleimide CO). In the proton NMR spectrum (DMSO-d_6 TMS), there is a doublet at 3.58 ppm (POMe, J(HP) 10.8 Hz), and for the olefinic protons of the maleimide, the AB part of an ABX system (which collapses to an AB spectrum by saturating the ^{31}P nucleus) with the following parameters: δ_A 3.83, δ_B 3.71 ppm and J_{AB} 9.6 Hz. This very high value of J_{AB} is unexpected and unexplained.



(I)



(II)

Complex II shows strong IR bands (CS_2) at 1876, 1726 and 1679 cm^{-1}. The NMR (pyridine-d_5; TMS) spectrum shows a singlet at 2.00 ppm (9H, Ar—CH_3) and a doublet at 4.96 ppm (3H, Ar—H, J(HP) 2.2 Hz), both signals being temperature-independent. The lines due to the diastereotopic olefinic protons of the maleimide ligand are temperature-dependent, and in a rather complex way; the relevant data are listed in Table 1. Here again, the maleimide protons are diastereotopic, proving the chirality of the molecule.

On cooling, the B proton is shifted upfield, but its coupling with the phosphorus remains unchanged; on the contrary, the coupling of proton A with the phosphorus drops sharply while its chemical shift is unaffected. All these changes are reversible.

The origin of these temperature-dependences is difficult to ascertain. The data clearly show that we are dealing with averaged shifts and couplings; the simplest interpretation seems to be that there is a very fast rotation of the maleimide ligand which converts one rotamer into the other, the relative amounts of both structures being temperature-dependent. There is, however, no Karplus-type equation known relating the couplings with the angles in a

TABLE 1

TEMPERATURE-DEPENDENCE OF THE NMR SPECTRUM OF OLEFINIC MALEIMIDE PROTONS IN $(C_6H_3Me_3)Cr(CO)[P(OMe)_3][$*N*-phenylmaleimide$]$

(Solvent: pyridine-d_5: TMS)

T(°C)	δ_A	δ_B	$\Delta\delta$	$\lvert J_{AP}\rvert$	$\lvert J_{BP}\rvert$	$\lvert J_{AB}\rvert$
32.5	3.84	3.48	0.36	1.7	4.4	4.8
21.0	3.84	3.51	0.33	1.2	4.4	4.8
− 2.0	3.85	3.61	0.24	0.0	4.4	4.8
−28.0	3.88	3.74	0.14	0.0	4.5	4.8

P—M—olefin system, and any attempt to correlate the data with definite structures seems to be bound to fail. Moreover, there may be more than two structures, and our results do not exclude three or even more rotamers, which makes the situation still less clear.

The other lines in the spectrum are insensitive to temperature changes.

It should be noted too that the mesitylene methyl groups of complex II give a single sharp resonance, even at 270 MHz at −28°, showing that the rotation around the Cr—Ar bond is very fast, despite the bulkiness of the substituents on the metal atom.

Experimental

Photolyses

Photolyses were run in Pyrex flasks with a Philips HPK 125 W medium pressure mercury arc. The benzene solutions were thoroughly degassed (residual pressure less than 10^{-3} mm Hg) prior to irradiation by numerous freeze—pump—thaw cycles, and again degassed at frequent intervals (every 30 min) during the photolysis to remove the carbon monoxide.

The isolation of the chiral complexes proved to be very difficult, and was achieved only by fast adsorption chromatography on alumina or silicagel; the elution was accelerated by pumping at the lower end of the column. The irradiated benzene solutions were concentrated and the residue placed on the column, which was eluted first with cyclohexane and then with a steep gradient of cyclohexane/ether, yielding the arene tricarbonyl and the arene dicarbonyl phosphite complexes. The solvent was then changed to ether/acetone 9/1, giving the chiral complex. Pure acetone elutes the arene dicarbonyl maleimide molecules. It should be noted that whatever photolysis method is used, all four complexes are produced when the tricarbonyl derivatives are irradiated.

Although the whole separation takes less than 20 min, the material balance shows losses amounting to some 50%. The reddish-brown crystals of the chiral complexes are reasonably stable only if kept cool and under nitrogen.

Analyses (NPhMI = *N*-phenylmaleimide): *Complex I*, found: C, 51.9, H, 4.9. $C_6H_6Cr[P(OCH_3)_3](CO)[NPhMI]$ (mol. wt. 455) calcd.: C, 52.8, H, 4.9%; *Complex II*, found: C, 65.8, H, 5.2. $[C_6H_6(CH_3)_3]Cr[P(OC_6H_5)_3](CO)[NPhMI]$ (mol. wt. 663) calcd.: C, 66.8, H, 5.1%.

NMR spectra were recorded on Varian A60 (60 MHz) and Brucker HFX270 (270 MHz) in DMSO-d_6 or pyridine-d_5.

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