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Preliminary communication

CHELATE ARENEOLEFINDICARBONYLCHROMIUM COMPLEXES

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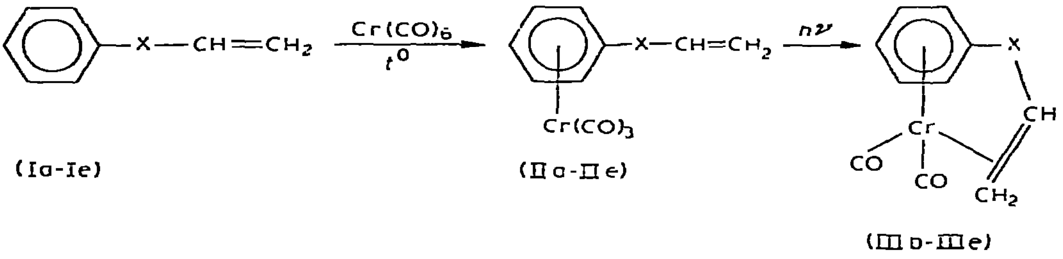
Summary

The preparation of the new type of chromium chelate complexes with polydentate ligands containing both a phenyl ring and an olefinic double bond is reported. The most stable complexes were found to be those in which the phenyl ring and the olefinic group were separated by a bridge consisting of 2 or 3 atoms.

As is known, the introduction of an electron-withdrawing group in the olefin molecule increases the stability of the (arene)$Cr(CO)_2$(olefin) complexes; These derivatives have been well studied [1-3]. On the other hand, a number of compounds of this type, in which the olefin has no electron-withdrawing group, is limited by examples where the olefins are ethylene [4, 5], cyclopentene or cycloheptene [5]. Similar complexes are not formed with propylene and other alkylolefins.

We have prepared new areneolefindicarbonylchromium complexes from polydentate ligands containing a phenyl ring and an olefinic double bond, by the route shown in Scheme 1.



a, X = CH_2; b, X = OCH_2; c, X = $(CH_2)_2$; d, X = $(CH_2)_3$; e, X = $(CH_2)_4$

The precursor organic ligands were obtained by conventional methods.

Treatment of I with $Cr(CO)_6$ in a boiling mixture of diglyme/n-octane (1/5) produced predominantly complexes II as pale yellow oils or solids. When complexes IIb-IIe are irradiated under UV light in petroleum ether the corresponding red chelate complexes III are formed, the progress of the reaction being monitored by IR spectroscopy in the metal-carbonyl region. Melting points and IR spectroscopic data of the investigated compounds are given in Table 1.

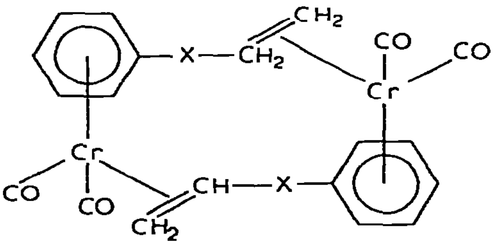
TABLE 1

IR SPECTRAL DATA AND MELTING POINTS OF COMPLEXES IIa-IIe AND IIIb-IIIe

	M.p. (°C)	$\nu(C\equiv O)$ (cm^{-1}) in cyclohexane
IIa	oil	1906, 1977
IIb	43-44	1905, 1976
IIc	19-20	1906, 1977
IId	oil	1909, 1977
IIe	oil	1906, 1978
IIIb	70-75 (dec.)	1885, 1938
IIIc	75-80 (dec.)	1878, 1930
IIId	75-80 (dec.)	1871, 1923
IIIe		1886, 1920

It should be emphasized, that areneolefinchromium complexes were isolated in cases where a double bond was separated from the arene ring by two (IIIb, IIIc) or three (IIId) atoms. When there are four atoms between the phenyl ring and the olefinic group the complex which forms (IIIe) is very unstable. Its formation was proved by IR spectroscopy and in its reaction with triphenylphosphine to produce the corresponding arenedicarbonyltriphenylphosphinechromium complex. UV irradiation of the solution of IIa, where the phenyl ring is separated from the double bond by one methylene group did not bring about the formation of compounds of type III but only resulted in gradual decomposition of the initial complex.

The formation of areneolefindicarbonylchromium complexes was not observed even by IR spectroscopy upon irradiation of arenetricarbonylchromium compounds in the presence of alkylolefins according to the literature [5]. This stability increase of the areneolefindicarbonylchromium complexes of type III we attribute to the chelate effect. Another possibility of intermolecular coordination to produce compounds of type IV is excluded in virtue of the chemical data



(IV)

and molecular weight values of the compounds IIIb-IIId, which are 236(242), 233(240), 244(254), accordingly (in brackets are listed calculated values). Molecular weights determined cryoscopically in benzene show that these compounds are monomeric in solution. All the compounds obtained are characterized by elemental analysis (C, H, Cr). Structural conformation by PMR spectra is now under investigation.

It should be noted that in the conversion of IIIb to IIIe, a gradual decrease of frequencies $\nu(C\equiv O)$ of the former complexes is observed which may be due to a change in the chelate cycle strain.

References

1 J.F. Guttenberger and W. Strohmeier, Chem. Ber., 100 (1967) 2807.
2 R.J. Angelici and L. Busetto, Inorg. Chem., 7 (1968) 1935.
3 (a) M. Herberhold and C. Jablonski, J. Organometal. Chem., 14 (1968) 457; (b) M. Herberhold and C. Jablonski, Inorg. Chim. Acta, 7 (1970) 241.
4 E.O. Fischer and P. Kuzel, Z. Naturforsch. B, 16 (1961) 475.
5 (a) W. Strohmeier and H. Hellmann, Chem. Ber., 98 (1965) 1598;
(b) W. Strohmeier and H. Hellmann, Ber. Bunsenges. Phys. Chem., 69 (1965) 178.