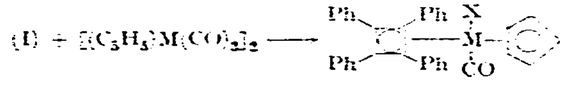
Cyclobutadiene–metal complexes

V*. (π-Cyclopentadienyl)(π-tetraphenylcyclobutadiene)molybdenum and -tungsten carbonyl halides

In parts I and II of this series we described a general synthesis of tetraphenylcyclobutadiene–metal complexes by reaction of metal carbonyls with tetraphenylcyclobutadienepalladium halides (I)[1,2] in which transfer of the cyclobutadiene ligand took place. We have also examined the reactions of substituted metal carbonyls such as the cyclopentadienyl metal carbonyls with (I). In this case the reaction can follow one of two paths, (*a*) the tetraphenylcyclobutadiene group can be transferred from palladium onto the other metal, or (*b*) the cyclopentadienyl group can be transferred onto palladium. The particular path taken by a system will depend on the relative strengths of the metal–ring bonds, amongst other factors, and can be used as a qualitative measure of the strengths of these bonds. Thus, reaction of cyclopentadienyliron dicarbonyl dimer (II) with (I) follows path (*b*) and gives mainly salts of the (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)palladium cation (III)[3]. The reactions of (II) with tetraphenylcyclobutadienenickel bromide or tetraphenylcyclobutadienecobalt dicarbonyl bromide also follow path (*b*)[3].

$$\underset{\text{(I)}}{(Ph_4C_4)PdX_2} + \underset{\text{(II)}}{[(C_5H_5)Fe(CO)_2]_2} \longrightarrow \underset{\text{(III)}}{[(Ph_4C_4)Pd(C_5H_5)]^+\ FeX_4^-}$$



(IV) (V)

In contrast, reaction of (I) with cyclopentadienylmolybdenum tricarbonyl dimer (IV, M = Mo) followed path (*a*) to give the (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)molybdenum carbonyl halides (V, M = Mo, X = Br, Cl). This reaction like the others could only be carried out under heterogeneous conditions. The best yield (18 %) was obtained from (I, X = Cl) and (IV, M = Mo) in refluxing xylene; variations on the procedure gave lower yields. It was also possible to prepare (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)tungsten carbonyl bromide (V, M = W, X = Br), the first characterized cyclobutadiene–tungsten complex[2], but only in very low yields (0.7 %) by a similar reaction in benzene.

The molybdenum complexes (V, M = Mo, X = Cl, Br) were air-stable red-brown crystalline solids, which were, however, rather heat- and air-sensitive in solution making recrystallization difficult. The NMR spectrum of the chloride (V, M = Mo, X = Cl) showed it to be diamagnetic and indicated the presence of phenyl protons and cyclopentadienyl protons in the expected ratio (20:5). The infra-red spectrum showed a carbonyl stretching band at 1973 cm^{-1} and was otherwise very similar to the spectra of the other (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)-metal complexes[1,3], in confirmation of the structure. The infra-red spectra of (V, M = Mo, X = Br) and (V, M = W, X = Br) were identical to the above showing that these complexes too had the same structure.

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[*] Parts III and IV, see ref. 3.

The fact that these reactions follow route (*a*) whereas those involving cyclopentadienyliron dicarbonyl dimer follow route (*b*) emphasizes again the greater strengths of the π-C_5H_5–Mo and π-C_5H_5–W bonds compared with the π-C_5H_5–Fe bond in these compounds. This is also illustrated by the well-known thermal conversion of (II) to ferrocene[4], a reaction which has no analogue in the molybdenum series. The low yields obtained in these reactions further emphasize the lower reactivity of the cyclopentadienylmolybdenum and -tungsten carbonyl dimers. Although the insoluble residues from the reactions were not extensively studied, infra-red spectra suggested the presence of large amounts of octaphenylcyclooctatetraene (formerly erroneously thought to be octaphenylcubane[5]). Since no (I) could be recovered this suggested that (I) was efficiently dehalogenated by (IV) but that substitution of (IV) by the tetraphenylcyclobutadiene was the difficult step, dimerisation to the cyclooctatetraene occurring preferentially.

Attempts to degrade (V, M = Mo, X = Cl) with hydrogen chloride in the presence of air led only to recovery of the starting material. This is in contrast to the observation[6] that (π-allyl)(π-cyclopentadienyl)molybdenum dicarbonyl gave (π-cyclopentadienyl)molybdenum oxide dichloride under similar conditions. The failure of our compound to react similarly must be due to steric hindrance.

Experimental

Cyclopentadienylmolybdenum tricarbonyl dimer (IV, M = Mo) was prepared from molybdenum hexacarbonyl and dicyclopentadiene by the method of Hayter[7]. The tungsten compound (IV, M = W) was obtained in 60% yield on refluxing a mixture of 11 g tungsten hexacarbonyl and 40 ml dicyclopentadiene in 60 ml triglyme for 3 hours. On cooling, (IV, M = W) crystallized from the reaction mixture.

All melting points were taken in evacuated capillaries but are uncorrected.

(π-Cyclopentadienyl)(π-tetraphenylcyclobutadiene)molybdenum carbonyl chloride (V, M = Mo, X = Cl). (i) in xylene. Cyclopentadienylmolybdenum tricarbonyl dimer (IV, M = Mo) (0.75 g, 1.5 mmoles) was added to a refluxing suspension of 1.0 g (1.87 mmoles) of tetraphenylcyclobutadienepalladium chloride (I, X = Cl) in 50 ml xylene. Refluxing was continued with vigorous stirring for ten minutes, the mixture was then filtered and the filtrate chromatographed on Florisil. A small amount of dimer (IV, M = Mo) was slowly eluted in xylene and benzene and completely removed with dichloromethane in benzene. A red band now slowly moved down and was eluted with ether as a red solution. The solvent was removed on a rotary evaporator at 25°, light petroleum, b.p. 80–100°, was added to give analytically pure red-brown crystals of (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)molybdenum carbonyl chloride (V, M = Mo, X = Cl), m.p. 261–266° (decomp.). Yield 200 mg, 18% based on (I). (Found: C, 70.16; H, 4.52; Cl, 6.34; Mo, 16.43; O, 3.12, 3.39; mol. wt., 619. $C_{34}H_{25}$-ClMoO calcd.: C, 70.28; H, 4.34; Cl, 6.10; Mo, 16.51; O, 2.75%; mol. wt., 581.) The compound in CCl_4 solution had ν_{CO} 1973 cm^{-1}; the NMR spectrum in $CDCl_3$ solution showed a fairly broad peak centred at 2.68 τ due to the phenyl protons and a sharp resonance at 4.55 τ due to the cyclopentadienyl protons. The intensity ratio was the expected 20:5.

(ii) in benzene. Tetraphenylcyclobutadienepalladium chloride (2.7 g, 5.0 mmoles) and 1.5 g (2.5 mmoles) of cyclopentadienylmolybdenum tricarbonyl dimer were refluxed in 200 ml of benzene for 50 hours under nitrogen with stirring. The hot

reaction mixture was filtered, the filtrate reduced in volume to 40 ml and then chromatographed on alumina. Excess dimer (IV) was eluted in benzene, and the desired product (V, M = Mo, X = Cl) was then eluted in ether. Yield 0.165 g, 5.5 % based on (I), of red-brown crystals with the same melting point and infra-red spectrum as those obtained by method (*i*).

(π-Cyclopentadienyl)(π-tetraphenylcyclobutadiene)molybdenum carbonyl bromide (IV, M = Mo, X = Br). This was obtained in 7 % yield by method (*i*) above and in 4.5 % yield, both based on (I), by method (*ii*) above, as red-brown crystals, m.p. 248–250° (decomp.). The infra-red spectrum was identical to that of the chloride (IV, M = Mo, X = Cl) and showed ν_{CO} at 1998 cm^{-1} (KBr disc). (Found: C, 65.06; H, 4.20; mol. wt., 620. $C_{34}H_{25}BrMoO$ calcd.: C, 65.29; H, 4.03 %; mol. wt., 625.)

(π-Cyclopentadienyl)(π-tetraphenylcyclobutadiene)tungsten carbonyl bromide (V, M = W, X = Br). Attempts to prepare this by method (*i*) were unsuccessful; method (*ii*) gave a 0.7 % yield of orange-yellow crystals of (π-cyclopentadienyl)-(π-tetraphenylcyclobutadiene)tungsten carbonyl bromide, m.p. 227–228° (decomp.). The infra-red spectrum was identical to those of the molybdenum complexes above with ν_{CO} at 1958 cm^{-1} (KBr disc). (Found: C, 57.35; H, 3.80; mol. wt., 700. $C_{34}H_{25}BrOW$ calcd.: C, 57.20; H, 3.54 %; mol. wt., 713.)

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