Journal of Organometallic Chemistry, 215 (1981) C30—C32
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

A CONVENIENT ENTRY INTO DIRUTHENIUM CHEMISTRY

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(Received May 6th, 1981)

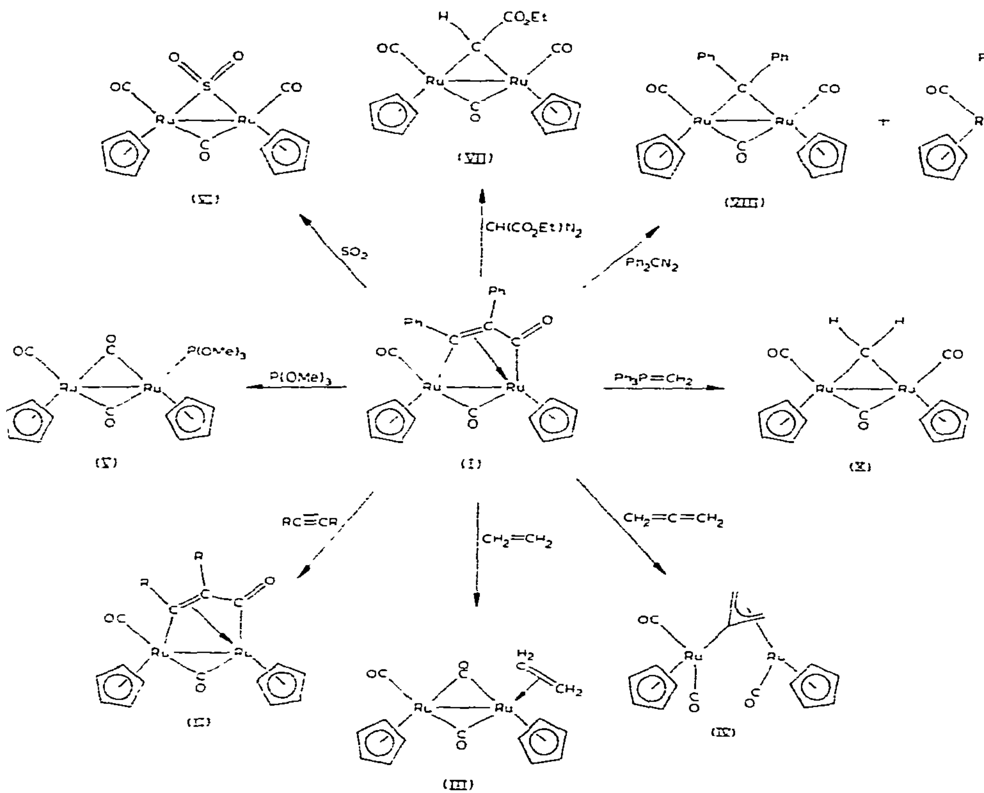
Summary

In boiling toluene, diphenylacetylene is readily displaced from the dimetallocycle $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ by a variety of reagents ($P(OMe)_3$, SO_2, R_2CN_2, Ph_3PCH_2) to produce $[Ru_2(CO)\{P(OMe)_3\}(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ or $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}L)(\eta\text{-}C_5H_5)_2]$ ($L = SO_2$, CR_2, CH_2) in high yield.

We recently described [1] the synthesis of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (I) by UV irradiation of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with diphenylacetylene, a 50% yield being commonly achieved. The complex is fluxional, undergoing a rapidly reversible breaking and regeneration of the C_2Ph_2—CO bond. However, at boiling toluene temperature the C_2Ph_2—CO link is broken irreversibly in the presence of other reagents, which displace the diphenylacetylene and enter into coordination with the $Ru_2(CO)_3(\eta\text{-}C_5H_5)_2$ unit. We have previously referred briefly to the formation of acetylene (II), ethylene (III) and allyl (IV) complexes in this way [1, 2], and now report that the route may be extended to provide an apparently general and very convenient entry into diruthenium chemistry which would otherwise be inaccessible because of the low reactivity of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ itself.

Each of the reactions outlined in Scheme 1 occurs very rapidly in boiling toluene, reaching completion within minutes and providing the products in very high yield after chromatographic purification.

At a rather trivial level, phosphorus ligand complexes such as V may be obtained and appear from the IR spectrum to exist as the carbonyl-bridged isomer illustrated ($\nu(CO)(CH_2Cl_2)$: 1953s and 1733s cm^{-1}), analogous to the terminally bound ethylene complex III [2, 3]. Of more importance is the formation of the bridging sulphur dioxide complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SO_2)(\eta\text{-}C_5H_5)_2]$ (VI) as a yellow crystalline air-stable substance in 88% yield. The IR spectrum has carbonyl bands at 2029s, 1998m, and 1817m cm^{-1}, indicative of a structure



SCHEME 1

with pairs of *cis*-carbonyl and cyclopentadienyl ligands, and there is, in accordance, a single ^{1}H NMR signal at τ 4.30 between +30 and −70°C. Recently, Herrmann et al. [4] have reported the formation of a μ-SO_2 complex of dirhodium $[Rh_2(CO)_2(\mu\text{-}SO_2)(\eta\text{-}C_5H_5)_2]$ and drawn attention to the analogy with μ-carbene complexes. Diruthenium μ-carbene complexes are very reactive [5] and the chemistry of VI is under exploration in an extension of these studies.

Our investigations of the reactivity of μ-carbene complexes have relied chiefly on species derived [2, 3] in several steps from II and IV. Reactions of I with diazo compounds provide related complexes more directly, but a thermally fairly robust diazoalkane is required. For example, $CH(CO_2Et)N_2$ and Ph_2CN_2 do not react with I at room temperature, but do so rapidly under toluene reflux to afford VII (78%) and VIII, respectively. IR (ν(CO)(CH_2Cl_2): 1994s, 1959s. 1792s cm^{-1}) and ^{1}H NMR spectra of VII identify the presence of both *cis* (τ ($CDCl_3$), 0.73 (s, 1H), 4.72 (s, 10H), 5.88 (q, *J* 8 Hz, 2H), 8.78 (t, *J* 8 Hz, 3H)] and *trans* [τ ($CDCl_3$), 1.56 (s, 1H), 4.68 (s, 5H), 4.74 (s, 5H), 5.80 (q, *J* 8 Hz, 2H), 8.64 (t, *J* 8 Hz, 3H)) isomers but for VIII only a *cis* isomer appears to be present (ν(CO)(CH_2Cl_2): 1986s, 1942m, and 1798m cm^{-1} ; ^{1}H NMR (CD_2Cl_2): τ 2.35—3.20m (10 H), 4.90s (10 H)). Crowding within VIII is evidently severe, because under the conditions of the synthesis decarbonylation occurs to provide IX as a coproduct (ν(CO)(CH_2Cl_2): 1939s, 1764m cm^{-1} ; ^{1}H NMR ($CDCl_3$) τ 2.3—3.6m (9H), 5.14s (5H), 5.56s (5H), and 7.54 (dd, *J* 7 and 1 Hz, 1H)).

The high field shift we attribute to the proton attached to the coordinated "olefinic" bond. A very related form of this CPh_2 bridging has been observed by Curtis et al. in a dimolybdenum complex [6].

Thermally very unstable diazomethane provides no product with I, but the phosphorus ylid $Ph_3P{=}CH_2$ smoothly generates air-stable yellow crystalline $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ (X) as a mixture of *cis* and *trans* isomers in 70% combined yield. The isomers, which may be separated by chromatography, equilibrate rapidly in $CDCl_3$ solution to achieve a *cis/trans* ratio of ca. 2/1. For the thermodynamically more stable *cis* isomer the ^1H NMR spectrum has signals at τ 0.84 (s, 1H), 2.48 (s, 1H), and 4.76 (s, 10H), and for the *trans* at τ 1.56 (s, 2H) and 4.68 (s, 10H). The chemistry of this μ-CH_2 complex, the most important member of the series of μ-carbene diruthenium complexes, is under active investigation. The wide range of phosphorus ylids available suggests that this route will be important in the synthesis of μ-carbene complexes.

We are grateful to the S.R.C. for the award of Research Studentships (to D.L.D. and A.F.D.) and for support, and to Johnson Matthey and Co. Ltd., for a loan of ruthenium trichloride.

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