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Preliminary communication

CONVERSION OF ALLENE INTO μ-DIMETHYLCARBENE AT A DIRUTHENIUM CENTRE

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Summary

Treatment of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ with allene in toluene at 100°C displaces diphenylacetylene and produces $[Ru(CO)(\eta\text{-}C_5H_5)\{\eta^3\text{-}C_3H_4Ru(CO)_2(\eta\text{-}C_5H_5)\}]$; upon protonation a 1-methylvinyl cation $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me)CH_2\}(\eta\text{-}C_5H_5)_2]^+$ is formed which undergoes nucleophilic attack by hydride to yield the μ-dimethylcarbene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$.

The transition metal chemistry of μ-carbenes [1] is of interest because of the possible involvement of such species in Fischer—Tropsch synthesis [2], alkene metathesis and alkyne polymerisation [3]. Synthetic routes to μ-carbene complexes, especially simple hydrocarbon varieties, are not numerous and we are therefore prompted to communicate a new route which provides μ-dimethylcarbene. It involves an unprecedented conversion of allene.

The dimetallocycle $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (I), which is readily obtained by the photochemical reaction of diphenylacetylene with $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, has been reported to undergo quantitative alkyne exchange when heated with ethyne or but-2-yne in toluene [4]. When heated under the same conditions with allene, diphenylacetylene is again liberated, in a reaction which provides $[Ru(CO)(\eta\text{-}C_5H_5)\{\eta^3\text{-}C_3H_4\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)\}]$ (II) quantitatively as very soluble pale yellow crystals. IR and ^1H NMR spectra indicate that the product must be formulated as an η^3-allyl complex of the $Ru(CO)(\eta\text{-}C_5H_5)$ fragment, but with σ-bound $Ru(CO)_2(\eta\text{-}C_5H_5)$ as a 2-allyl substituent; i.e. allene enters into coordination with the $Ru_2(CO)_3(\eta\text{-}C_5H_5)_2$ unit provided by I to bridge the two metal atoms and remove metal—metal bonding. Precedent for II exists in the complex $[Fe_2(CO)_7(C_3H_4)]$ (V) [5, 6].

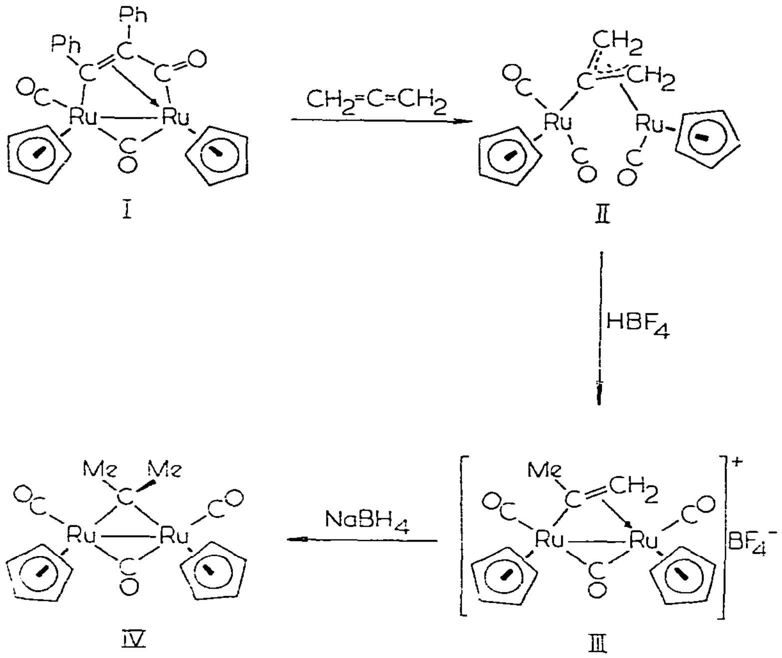
Three strong (2023, 1967, 1945) and three weak (2034, 1976, 1953 cm^{-1} (hexane)) terminal carbonyl stretching frequencies are observed in the IR spectrum of II. We attribute these to the existence of two rotamers, arising from a restricted rotation about the Ru—η^3-allyl bond, of the type suggested previously for the unsubstituted allyl complex [Ru(CO)(η^3-C_3H_4)(η-C_5H_5)] [7]. The introduction of the very bulky Ru$(CO)_2$(η-C_5H_5) substituent into the η^3-allyl group will ensure that rotation is at least as restricted in II. In fact, it appears to be slow even on the NMR time scale, in that the ^{1}H NMR spectrum of II comprises an intense set of signals due to a major rotamer (τ 4.63 (s, 5 H), 4.94 (s, 5 H), 7.19 (m, 2 H), 8.57 (m, 2 H) ($CDCl_3$)) and a weak set of accompanying signals at slightly lower field for the minor rotamer. For the *syn* and *anti* allylic protons the latter appears only as shoulders, but for the η-C_5H_5 groups the signals are resolved at τ 4.62 and 4.93.

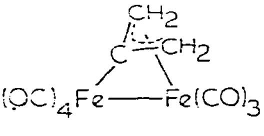
Acidification of II with HBF_4 in ether causes quantitative precipitation of the μ-1-methylvinyl complex [$Ru_2(CO)_2$(μ-CO){η-C(Me)CH_2}(η-C_5H_5)$_2$] [BF_4] (III) as a lemon-yellow powder. Characterisation was facilitated by the previous identification and structural elucidation of the μ-vinyl analogues [$M_2(CO)_2$(μ-CO)(μ-CHCH_2)(η-C_5H_5)$_2$] [BF_4] (M = Fe or Ru) [8]. Like these, complex III exists as a mixture of *cis* and *trans* isomers, revealed by the IR spectrum which has ν(CO) at 2036s, 2015vs and 1867s, (br) cm^{-1} (CH_2Cl_2) and by the ^{1}H NMR spectrum, which at −30°C has two sets of signals in an intensity ratio of ca. 3.2. The major isomer (which we believe to be the *trans*) has signals at τ 4.29 (s, 5 H), 4.16 (s, 5 H), 5.08 (d, J 1 Hz, 1H), 6.39 (d, J 1 Hz, 1 H), 6.67 (s, 3 H) and the minor isomer signals at τ 3.91 (s, 5 H), 4.06 (s, 5 H), 5.28 (d, J 1 Hz, 1 H), 6.54 (s, 3 H), 6.87 (d, J 1 Hz, 1 H) in acetone-d_6. On warming, coalescence of signals occurs in accord with the onset of a combination of *cis—trans* interconversion and the established [9] fluxional rearrangement of a μ-vinyl ligand. It is noteworthy that in the transformation of II to III the ruthenium—ruthenium bond lost in going from I to II is regenerated.

Treatment of III with sodium borohydride in acetone at −78°C effects nucleophilic attack by hydride specifically upon the β-vinylic carbon, producing the yellow crystalline μ-dimethylcarbene complex [$Ru_2(CO)_2$(μ-CO)(μ-CMe_2)(η-C_5H_5)$_2$] (IV) in 60%yield. Both *cis* and *trans* isomers are again indicated by the IR spectrum (ν(CO) 1988s, 1953(sh), 1947s (br), 1800s cm^{-1} (hexane) and at 30°C in $CDCl_3$ these are seen in the ^{1}H NMR spectrum to co-exist, without interconverting, in a *cis/trans* ratio of ca. 2/3. For the *cis* isomer signals are at τ 4.80 (s, 10 H), 6.94 (s, 3 H), 6.99 (s, 3 H) and for the *trans* at τ 4.84 (s, 10 H), 6.86 (s, 6 H). The behaviour of the isomers at elevated temperatures is under investigation.

The sequence I→II→III→IV represents a convenient high yield (effectively 60%) route to μ-dimethylcarbene via a unique transformation of allene. Substituted allenes are available and we anticipate being able to convert these analogously (e.g. buta-1,2-diene to μ-C(Me)Et and penta-2,3-diene to μ-CEt_2). It may be noted, finally, that the reaction of complex I marks it as an "$Ru_2(CO)_3$(η-C_5H_5)$_2$" source. This was confirmed when bubbling ethylene through a boiling toluene solution of I generated [Ru_2(CO)(C_2H_4)(μ-CO)$_2$(η-C_5H_5)$_2$] (VI) rapidly in ca. 70% yield. This complex had previously only been available to us in trace amounts by another route [7].

Further reactions of I with a variety of unsaturated hydrocarbons are under investigation.





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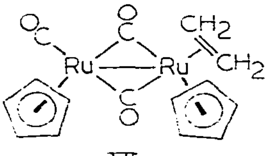

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