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Preliminary communication

A NOVEL SIX-MEMBERED RUTHENIUM METALLOCYCLE

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Summary

Treatment of dihydridocarbonyltris(triphenylphosphine)ruthenium with methyl propiolate affords a six-membered ruthenium metallocycle which is characterized by X-ray crystal analysis.

Formation of metallocyclopentadiene complexes by the reaction of transition metal complexes with acetylenes is observed frequently and their important roles in oligomerization of acetylenes are well established [1]. In this report, we describe the formation of a novel six-membered metallocycle from a reaction of this type.

A mixture of dihydridocarbonyltris(triphenylphosphine)ruthenium (I) and methyl propiolate (1:6 molar ratio) in benzene was heated at 80°C under nitrogen during 1 hr to give an air stable, red violet, crystalline compound with empirical formula $Ru(CO)(PPh_3)_2(HC_2CO_2CH_3)_3$ (II) [m.p. 189–190°C, 25% yield, IR spectrum ν(CO) 1940 cm^{-1}, NMR spectrum($CDCl_3$) δ 3.20, 3.50, 3.60 ppm (s, 3H each) 6.10 (t, J 3 Hz, 1H, reduced to a singlet by ^{31}P decoupling) 11.67 (quart., J 1.5 Hz, 1H, reduced to a doublet by ^{31}P decoupling) 7.2–7.5 (complex, phenyl protons probably including one olefinic proton)].

The data obtained did not establish the structure of II, and therefore, an X-ray crystal structure determination was undertaken.

The cell constants of the crystals of II were determined from a least-squares refinement of the setting angles of 13 reflections with 2θ range of 40-70° centered on a Rigaku computer-controlled diffractometer. Crystal data: $\underline{a}$=11.118(5), $\underline{b}$=19.926(7), $\underline{c}$= 11.518(5)Å; $\underline{\alpha}$=104.09(3), $\underline{\beta}$=119.66(3), $\underline{\gamma}$=87.61(3)°; space group triclinic $\underline{P}\bar{1}$; $\underline{Z}$=2; $\underline{D}$m=1.41, $\underline{D}$c=1.40 g/cm^3. Intensity data were collected by the 2θ-ω scan method using Cu $\underline{K}\alpha$ radiation up to 2θ of 120°. Anisotropic refinement of all nonhydrogen atoms

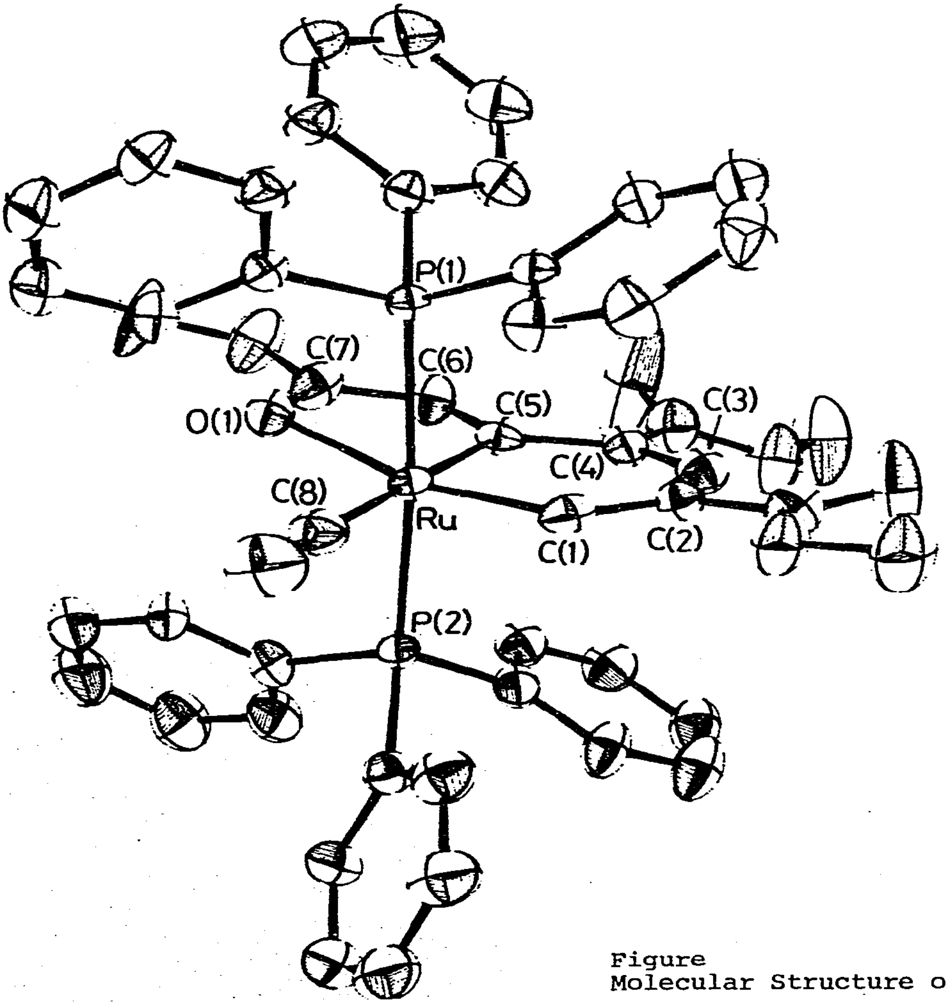


Figure
Molecular Structure of II

gave the final discrepancy factor R=0.034 for 6359 independent reflection data with $Fo > 3\sigma(Fo)$. A view of the molecule is given in the Figure.

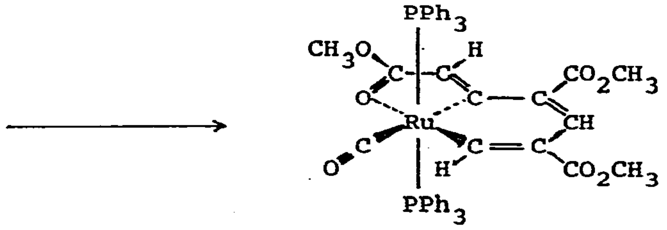
The relevant bond length are: Ru-P(1), 2.383(2); Ru-P(2), 2.362(2); Ru-C(1), 2.003(11); Ru-C(5), 2.107(7); Ru-C(8), 1.909(8); Ru-O(1), 2.260(7); C(1)-C(2), 1.367(12); C(2)-C(3), 1.448(10); C(3)-C(4), 1.340(13); C(4)-C(5), 1.477(12); C(5)-C(6), 1.369(14); C(6)-C(7), 1.442(14); C(7)-O(1), 1.239(9)Å.

The coordination sphere about the ruthenium is approximately octahedral. The interesting structural feature of II is the existence of a six-membered metallocyclohexadiene ring consisted of three methyl propiolate molecules and a ruthenium, instead of a simply immaginable seven-membered metallocycloheptatriene ring.

The complex forming reaction may proceed via (1) formation of coordinatively unsaturated species such as III, (2) oxidative addition of methyl propiolate to give a hydridoethynylruthenium complex, IV, (3) 1,3-hydrogen shift to form a vinylideneruthenium complex, V, and (4) ring expansion by successive addition of two molecules of methyl propiolate. The dehydrogenation of I to give III is suggested by gas chromatographic detection of methyl acrylate, the hydrogenation product of methyl propiolate, and by the absence of original dihydrido moiety in II as evidenced by the use of 3-deuterio methyl propiolate. While there is no direct evidence for IV, the corresponding compound $Ru(H)(C{\equiv}CBu^t)(CO)(PPh_3)_3$ was isolated from the reaction of I with t-butylacetylene at 80°C [m.p. ~135°C(decomp.), 21% yield, IR spectrum ν(Ru-H) 2010, ν(CO) 1938 cm^{-1}, NMR spectrum($CDCl_3$) δ -8.24 ppm (d.t., J(PH trans) 88, J(PH cis) 26 Hz, Ru-H), 0.57 (s, C_4H_9), 6.9-7.6 (complex, C_6H_5)]. The formation of V is also hypothetical. However, it is interesting in this connection that the reaction of $Mn(\eta\text{-}C_5H_5)(CO)_2(THF)$ with phenylacetylene was reported to give a phenylvinylidenemanganese complex $Mn(\eta\text{-}C_5H_5)(C{=}CHPh)(CO)_2$ [2]. Our recent finding of the catalytic formation of 1,4-di-t-butylbutatriene from t-butylacetylene in the presence of I also may show a great tendency for vinylidene type complex formation in the reaction of I with terminal acetylenes [3].

$$\underset{\text{I}}{Ru(H)_2(CO)(PPh_3)_3} \longrightarrow \underset{\text{III}}{\{Ru(CO)(PPh_3)_3\}} \longrightarrow$$

$$\underset{\text{IV}}{\{Ru(H)(C{\equiv}CCO_2CH_3)(CO)(PPh_3)_3\}} \longrightarrow \underset{\text{V}}{\{Ru(C{=}CHCO_2CH_3)(CO)(PPh_3)_3\}}$$



II

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