Synthesis and Some Reactions of the Rhodacyclopentadiene Complex $[Rh(CO)_2\{C_4(CO_2Me)_4Rh(CO)_2PPh_3)\}]$ [†]

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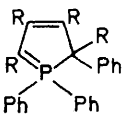
Electron-deficient alkynes, $RO_2CC_2CO_2R$ (R = H or Me), cyclotrimerize on heating in the presence of $[\{Rh(CO)_2(PPh_3)_2\}_2]$, but other alkynes RC_2R' (R = R' = H, Ph, Et, and CMe_2OH; R = Ph, R' = H) failed to react under similar conditions. From the reaction with $MeO_2CC_2CO_2Me$, have been isolated $[Rh_2(CO)_2(PPh_3)_4(MeO_2CC_2CO_2Me)]$ and the title compound $[Rh(CO)_2\{C_4(CO_2Me)_4Rh(CO)_2(PPh_3)\}]$. A possible mechanism for the cyclotrimerization reaction is discussed.

THE synthesis of the η-(iridacyclopentadienyl)iridium complex $[Ir(CO)_2\{C_4(CO_2Et)_4Ir(CO)_2(PPh_3)\}]$ recently reported[1] from the reaction of $[\{Ir(CO)_3(PPh_3)\}_2]$ with $EtO_2CC_2CO_2Et$ has prompted us to describe the results of a preliminary study carried out some years ago on the related reactions of alkynes with $[\{Rh(CO)_2(PPh_3)_2\}_2]$.

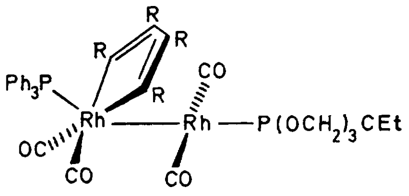
RESULTS AND DISCUSSION

When a suspension of $[\{Rh(CO)_2(PPh_3)_2\}_2]$ and a large excess of dimethyl acetylenedicarboxylate in benzene was heated at 80 °C for 21 h under a slow stream of carbon monoxide it gave hexamethyl benzenehexacarboxylate in 47% yield; this represents a ratio, mol of trimer : mol of rhodium complex, of 8.5 : 1. No catalyst could be recovered at the end of the reaction, only a brown, amorphous solid which contained rhodium and phosphine ligands, but was inactive catalytically. Under similar conditions acetylenedicarboxylic acid gave a low yield (14%, *i.e.* trimer : complex 4 : 1) of a white solid, which appears to be a dianhydride, or mixture of dianhydrides, of benzenehexacarboxylic acid on the basis of analytical and spectroscopic data. No reaction was observed between the rhodium dimer and acetylene, diphenylacetylene, hex-3-yne, phenylacetylene, and but-2-yne-1,4-diol under similar conditions.

Reaction between $MeO_2CC_2CO_2Me$ and the rhodium dimer at room temperature under 1 atm [‡] of CO in a sealed tube over 22 h gave bright orange crystals of a compound which analysed for $[Rh_2(CO)_4(PPh_3)(MeO_2CC_2CO_2Me)_2]$ in 25% yield based on available rhodium. The yield of this product was improved to 47% by carrying out the reaction at room temperature in benzene under a slow stream of carbon monoxide for 22 h. Chromatography and t.l.c. indicated that several other products were formed in this reaction, the major one being $PC_4(CO_2Me)_4Ph_3$ (1) (33% yield), a known[2] product of reaction between PPh_3 and $MeO_2CC_2CO_2Me$. On one occasion, a product which analysed as $[Rh_2(CO)_2(PPh_3)_4(MeO_2CC_2CO_2Me)]$ was isolated in 4% yield as an orange solid, but this was unstable in solution even under an atmosphere of nitrogen. There was insufficient of this compound for adequate characterisation, and we were unable to reproduce the conditions required for its isolation. By analogy with the well known cobalt complexes $[Co_2(CO)_6(alkyne)]$[3,4] and related rhodium complexes of the type $[Rh(CO)(alkyne)(\eta\text{-}C_5H_5)]$[5,6] this orange complex is expected to have the structure (2), in which the alkyne ligand bridges two $Rh(CO)(PPh_3)_2$ moieties.



(1)



(4)

$R = CO_2Me$

The i.r. spectrum of the complex $[Rh_2(CO)_4(PPh_3)(MeO_2CC_2CO_2Me)_2]$ [ν(C≡O) bands at 2 072vs, 2 044s, 2 030 (sh), and 1 998s, and ν(C=O) bands at 1 725s and 1 705ms cm^{-1}] shows a strong similarity with that of the complex $[Ir(CO)_2\{C_4(CO_2Et)_4Ir(CO)_2(PPh_3)\}]^1$ [ν(C≡O) 2 060s, 2 040s, 2 020s, and 1 970s; ν(C=O) at 1 720s and 1 680ms cm^{-1}]. The ^1H n.m.r. spectrum shows a complex multiplet at δ 7.37 p.p.m. for the aromatic protons, and sharp singlets at δ 3.66 and 3.42 for the $-OCH_3$ groups in the intensity ratio 15 : 6 : 6. On the basis of the spectroscopic evidence this compound is assigned the structure (3). Reaction of (3) with an equimolar amount of $P(OCH_2)_3CEt$ in toluene at room temperature gave an 82% yield of a complex $[Rh_2(CO)_4(PPh_3)\{P(OCH_2)_3CEt\}\{C_4(CO_2Me)_4\}]$ formed *without gas evolution*. The i.r. spectrum of this compound showed only three strong bands in the ν(C≡O) region at 2 060vs, 2 019s, and 1 991vs cm^{-1}, and ν(C=O) bands at

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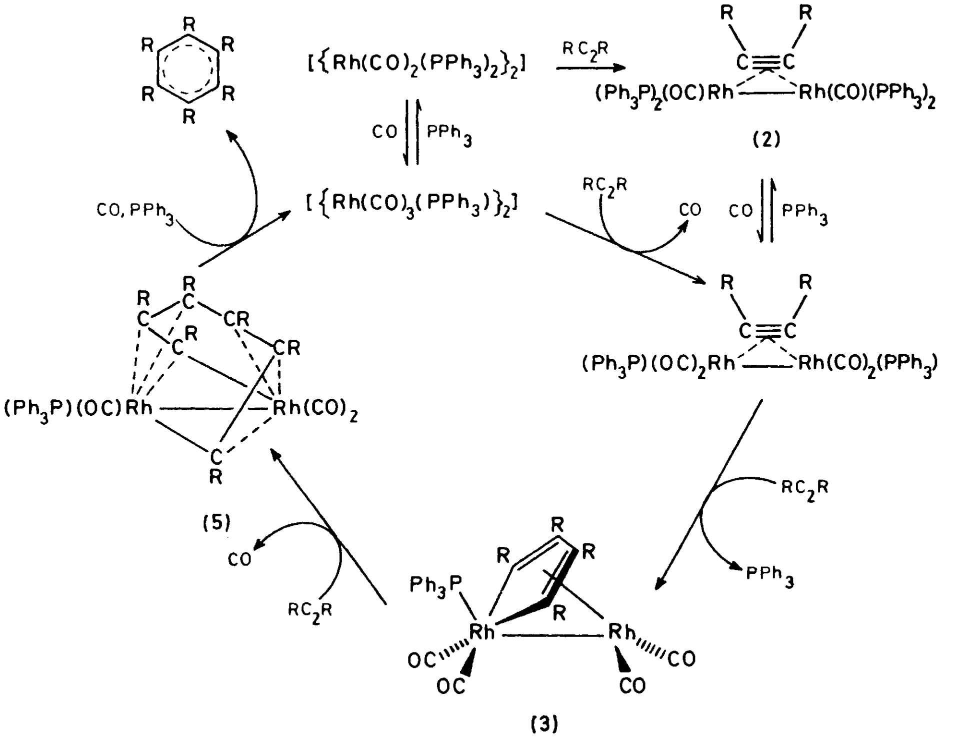
[†] 1,1,2,2-Tetracarbonyl-μ-[1′—4′-η-tetra(methoxycarbonyl)-buta-1′,3′-diene-1′,4′-diyl-$C^{1',4'}(Rh^1)C^{1'-4'}(Rh^2)$]-1-triphenylphosphinedirhodium (*Rh–Rh*).

[‡] Throughout this paper: 1 atm = 101 325 N m^{-2}.

1 729s and 1 700ms cm^{-1}. The ^{1}H n.m.r. spectrum showed bands at δ 7.36 (m, 15 H, PPh_3), 4.19 [d, 6 H, OCH_2, J(P–H) 5], 3.62 (s, 6 H, OCH_3), 3.38 (s, 6 H, OCH_3), 1.18 (quartet, 2 H, CH_2, J 7.5 Hz), and 0.78 (t, 3 H, CH_3). The absence of any virtual coupling between the PPh_3 and $P(OCH_2)_3CEt$ ligands suggests that they are substituted on different rhodium atoms, and the most likely structure is (4), in which the phosphite ligand has displaced the η^4-rhodacyclopentadiene ligand. The two carbonyl groups on this rhodium(I) atom must have a *trans* arrangement giving rise to only one strong absorption in the i.r. spectrum.



SCHEME R = CO_2Me

When a solution of dimethyl acetylenedicarboxylate and a small amount of (3) in benzene was heated under reflux for 5 h in an atmosphere of dry nitrogen it gave $C_6(CO_2Me)_6$ in 48% yield (trimer : rhodium complex 22.7 : 1). This suggests that (3) is a true intermediate in the cyclotrimerization of $MeO_2CC_2CO_2Me$ by $[\{Rh(CO)_2(PPh_3)_2\}_2]$. The first step in the catalytic cycle (see Scheme) is probably the known [7] reaction of $[\{Rh(CO)_2(PPh_3)_2\}_2]$ with carbon monoxide to give $[\{Rh(CO)_3(PPh_3)\}_2]$, which like the parent dimer [8] and $[Co_2(CO)_8]$[9] has bridging carbonyl ligands. The isolation of compound (2) from the reaction mixture suggests that reaction with alkyne competes with this reaction with carbon monoxide. The cyclotrimerization of alkynes by $[Co_2(CO)_8]$ is believed to proceed by successive formation of an η^2-alkyne complex $[Co_2(CO)_6(alkyne)]$, and a bis(allyl) 'fly-over' bridged complex $[Co_2(CO)_4(alkyne)_3]$.[3,4] It seems likely that the rhodium-catalyzed reactions described in this work proceed *via* similar intermediates, and that the isolated rhodacyclopentadiene complex (3) is a precursor to a 'fly-over' bridged intermediate (5). Bennett *et al.*[10] came to the same conclusion based on the results of their study of the reactions of alkynes with $[Rh_2(PF_3)_8]$ in which intermediates of the type $[Rh_2(PF_3)_6(alkyne)]$ and $[Rh(PF_3)_2\{C_4R_2R'_2Rh(PF_3)_3\}]$ ($R = R' = CO_2Me$; $R = CO_2Me$, $R' = H$) were isolated. Although the direct link between the intermediates (3) and (5) has not yet been firmly established it seems likely to involve prior co-ordination of the incoming alkyne ligand to the rhodium(I) atom of (3), giving an adduct similar to that formed with $P(OCH_2)_3CEt$ but with a *cis* rather than *trans* arrangement of the carbonyl ligands. Insertion of the co-ordinated alkyne ligand into the rhodacyclopentadiene ring would give a dirhodaocta-3,5,7-triene complex, followed by rearrangement of the six π electrons with loss of a CO ligand giving (5).

EXPERIMENTAL

Except where stated, i.r. spectra were recorded on Nujol and hexachlorobutadiene mulls using a Perkin-Elmer 257 instrument; the metal carbonyl region was recorded on solutions in CH_2Cl_2 using full scale expansion. Hydrogen-1 n.m.r. spectra were recorded on a Varian HA 100 instrument on solutions in $CDCl_3$ with $SiMe_4$ internal reference, and molecular weights were determined using a Mechrolab osmometer. Chromatographic separations were carried out on Florisilpacked columns. The alkynes used were all commercial samples purified by distillation or recrystallisation, and $[\{Rh(CO)_2(PPh_3)_2\}_2]$ was prepared by a previously reported procedure.[11]

Reactions of $[\{Rh(CO)_2(PPh_3)_2\}_2]$.—(*a*) *With* $MeO_2CC_2CO_2Me$ *at* 80 °C. A suspension of the rhodium dimer (0.8 g, 0.6 mmol) and the alkyne (4.5 g, 31.7 mmol) in benzene (50 cm^3) was heated under reflux for 21 h under a slow stream of carbon monoxide. Removal of the solvent gave a black solid (3.2 g) which was chromatographed (Et_2O eluant) to give hexamethyl benzenehexacarboxylate (2.1 g, 5.0 mmol, 47%) as white needles, m.p. 186 °C (lit.,[12] 187—188 °C). Further elution with methanol gave only a brown decomposition product (0.8 g).

(*b*) *With* $MeO_2CC_2CO_2Me$ *at room temperature.* Addition of the alkyne (0.8 g, 5.6 mmol) to a stirred suspension of rhodium dimer (0.8 g, 0.6 mmol) in benzene (50 cm^3) at room temperature under a slow stream of CO gave a homogeneous deep red solution after a few minutes. This was stirred for a further 22 h before removal of the solvent and chromatography of the orange-red solid residue (1.35 g). Elution with Et_2O gave orange crystals of (3) (0.2 g, 0.24 mmol, 47%) which was recrystallised from a 1 : 2 mixture of Et_2O–hexane, m.p. 118 °C (decomp.) (Found: C, 47.4; H, 3.3; P, 3.6. $C_{34}H_{27}O_{12}PRh_2$ requires C, 47.2; H, 3.1; P, 3.6%). Further elution with CH_2Cl_2 gave another orange solid (0.12 g, 4%) believed to be compound (2), m.p. 80 °C (decomp.) (Found: C, 66.0; H, 4.9. $C_{80}H_{66}O_6P_4Rh_2$ requires C, 66.1; H, 4.0%), and compound (1) (0.15 g, 33%) as a yellow solid, m.p. 254 °C (lit.,[2] 253—255 °C).

(*c*) *With acetylenedicarboxylic acid.* A solution of the rhodium dimer (0.8 g, 0.6 mmol) and acetylenedicarboxylic acid (5.0 g, 43.9 mmol) in benzene–acetone (1 : 1) was stirred and heated under reflux for 22 h under a slow stream of carbon monoxide. Removal of the solvent and chromatography (Et_2O) of the dark brown residue gave white crystals (0.61 g) thought to be a dianhydride of benzenehexacarboxylic acid, m.p. 195—197 °C (Found: C, 47.3; H, 0.9%; *M* 297 (EtOH). Calc. for $C_{12}H_2O_{10}$: C, 47.1; H, 0.7%; *M* 306); i.r. 1 800vs and 1 695vs cm^{-1} [ν(C=O)].

Reactions of Compound (3).—(*a*) *With* $P(OCH_2)_3CEt$. A solution of the phosphite (0.1 g, 0.6 mmol) in toluene (15 cm^3) was added dropwise to a stirred solution of (3) (0.15 g, 0.6 mmol) in toluene (30 cm^3) contained in a flask attached to a gas burette. The mixture was stirred at room temperature for 4 h during which time there was no gas evolution. Chromatography (Et_2O) of the red solution gave a trace of a purple solid, and further elution with acetone gave compound (4) (0.5 g, 82%) as an orange-red solid, m.p. 118—123 °C (decomp.), which was recrystallised from acetone–hexane (1 : 2) (Found: C, 46.6; H, 4.1. $C_{40}H_{38}O_{15}P_2Rh_2$ requires C, 46.8; H, 3.7%).

(*b*) *With* $MeO_2CC_2CO_2Me$. A mixture of (3) (0.18 g, 0.22 mmol) and the alkyne (4.4 g, 31.0 mmol) in benzene (50 cm^3) was stirred and heated under reflux for 5 h under a slow stream of nitrogen. Chromatography of the resulting black solution gave $C_6(CO_2Me)_6$ (2.12 g, 48%).

[1/825 *Received*, *22nd May*, 1981]

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