

CYCLOTRIMERIZATION OF ACETYLENES CATALYZED BY $(\eta^5\text{-CYCLOPENTADIENYL})\text{RHODIUM COMPLEXES}$

KHALID ABDULLA, BRIAN L. BOOTH*, and CATHERINE STACEY

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD (Great Britain)

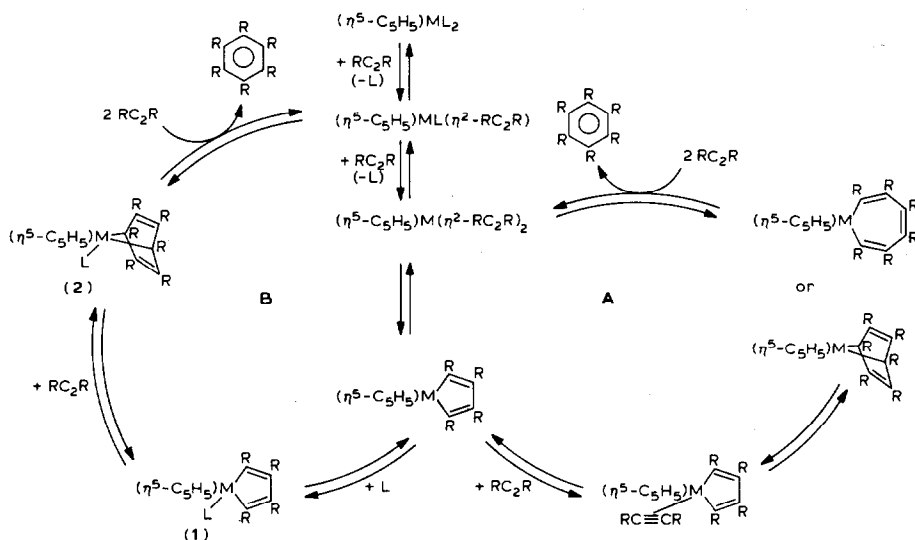
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Summary

The comparative rates of cyclotrimerization of dimethylacetylenedicarboxylate (DMAD) and hex-3-yne have been studied with the catalysts $[(\eta^5\text{-C}_5\text{R}_5)\text{Rh}(\text{COD})]$ ($\text{R} = \text{H}, \text{Me}, \text{Cl}$; $\text{COD} = \text{cycloocta-1,5-diene}$), $[(\eta^5\text{-C}_5\text{R}_5)\text{Rh}(\text{CO})_2]$ ($\text{R} = \text{H}, \text{Me}$), $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhL}_2]$ ($\text{L} = \text{C}_2\text{H}_4, \text{PF}_3$) and $[(\eta^5\text{-C}_5\text{H}_4\text{PPh}_3)\text{Rh}(\text{CO})_2]^+ \text{PF}_6^-$ under pseudo-first-order conditions. In these reactions, which all obey the rate law, $\text{rate} = k_{\text{obs}}[\text{acetylene}]$, the rate of cyclotrimerization of DMAD decreases as the π -acceptor strength of the cyclopentadienyl ligand increases, and this trend is reversed in reactions of hex-3-yne. The rates of cyclotrimerization also appear to vary with the nature of the ligand L (where $\text{L} = \text{C}_2\text{H}_4, \text{CO}, \text{PF}_3, \frac{1}{2}\text{COD}$) implying that L remains bound to the rhodium atom throughout the catalytic cycle. Preliminary studies have shown that in some cases selective co-oligomerization occurs with mixtures of two different acetylenes using the catalysts $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{COD})]$ and $[(\eta^5\text{-C}_9\text{H}_7)\text{Rh}(\text{COD})]$.

Introduction

There has been a great deal of recent interest in cyclotrimerization reactions of acetylenes catalyzed by η^5 -cyclopentadienylcobalt complexes [1–4]. To a large degree this stems from the imaginative use of this reaction for the synthesis of polycyclic compounds [2] and heterocycles [1,2,5]. Mechanistic studies [3,6,7] indicate that under thermal conditions these reactions can take place by the pathways shown in Scheme 1. The catalyst cycle **B**, which involves a direct Diels–Alder type of addition of the acetylene to a cobole intermediate of type **1**, has been demonstrated to occur when stoichiometric amounts of complex **1** ($\text{R} = \text{Me}, \text{L} = \text{PMe}_3$) and DMAD react at room temperature to give $\text{C}_6\text{Me}_4(\text{CO}_2\text{Me})_2$ [6], but how important this pathway is under catalytic conditions is not well established. It is usually assumed that in most reactions, and certainly when the mole ratio of



SCHEME 1

[acetylene]/ $[(\eta^5\text{-C}_5\text{H}_5)\text{CoL}_2]$ is large, the catalysis cycle A is followed and the ligand L plays no part in the reaction once the catalysis cycle is established [2,6,7].

The use of η^5 -cyclopentadienylrhodium complexes as catalysts for acetylene cyclotrimerization has not been studied in the same detail, and investigations have been restricted to experiments designed to isolate intermediate compounds using high concentrations of rhodium complex [8–13]. While these reactions are important, the results cannot necessarily be extrapolated to reactions in which the metal complex is present in only catalytic quantities. In order to investigate whether there is any significant difference in the catalytic behaviour of η^5 -cyclopentadienylcobalt and -rhodium complexes we have examined the rates of cyclotrimerization of DMAD and hex-3-yne using a variety of rhodium complexes of the type $[(\eta^5\text{-C}_5\text{R}_5)\text{RhL}_2]$ as catalysts and the results are now reported.

Results and discussion

The rates of cyclotrimerization of DMAD and hex-3-yne could not be followed conveniently either by ^1H NMR or IR spectroscopy, and all the reactions had to be monitored by taking small aliquots at intervals and measuring the rate of disappearance of the acetylene by GLC using dimethyldigol as an internal standard. Under pseudo-first-order conditions (acetylene/rhodium complex 100/1) the reaction of DMAD catalyzed by $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{COD})]$ at $109 \pm 0.1^\circ\text{C}$ in toluene gave a good straight-line plot of $\ln(a/a-x)$ vs. time for at least 95% conversion (Fig. 1). There was no evidence from GLC for any product other than hexacarbomethoxybenzene, and the measured rate of reaction was found to be reproducible ($\pm 4\%$) over six kinetic runs. A repeat of this reaction using three different catalyst concentrations (Table 1) gave a good straight-line plot of $\log(\text{initial rate})$ vs. $\log[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{COD})]$ of slope 0.97 indicating that the reaction was first order in [catalyst]. Also a plot of $\log k$ vs. $\log[\text{catalyst}]$ gave a straight line of slope 1.14

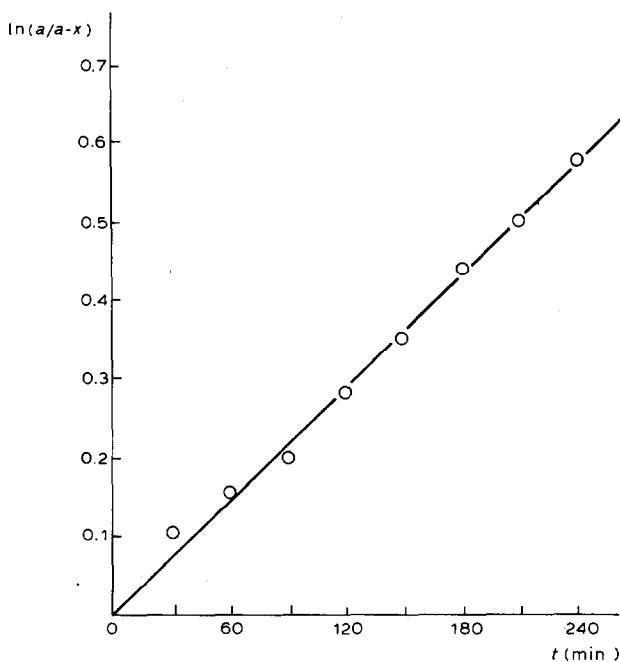


Fig. 1. Plot of $\ln(a/a-x)$ vs. time for the reaction of DMAD catalyzed by $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{COD})]$.

confirming that the reaction remains first order in catalyst throughout a run over the limited range of catalyst concentrations studied. The reaction of DMAD catalyzed by $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{COD})]$ was studied over five different acetylene concentrations and a plot of $\log(\text{initial rate})$ versus $\log[\text{acetylene}]$ gave a straight line slope of 1.18, confirming that the reaction is first order in $[\text{acetylene}]$. Each kinetic run was repeated five times (reproducibility $\pm 4\%$) and the results presented in Table 2 represent average values. Hence, these reactions obey the rate law

$$-\frac{d[\text{acetylene}]}{dt} = k[\text{acetylene}][\text{catalyst}]$$

The rates of cyclotrimerization of both DMAD and hex-3-yne have been measured under pseudo-first-order conditions ($[\text{acetylene}]/[\text{catalyst}]$ mole ratio 121/1) at the reflux temperature of toluene with the catalysts $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{COD})]$, $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{COD})]$ and $[(\eta^5\text{-C}_5\text{Cl}_5)\text{Rh}(\text{COD})]$. In all these reactions good first

TABLE 1

KINETIC RESULTS FOR THE REACTION OF $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{COD})]$ WITH DMAD IN TOLUENE AT $109 \pm 0.1^\circ\text{C}$

$10^3[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{COD})]$ (mol dm ⁻³)	$10^2[\text{DMAD}]$ (mol dm ⁻³)	10^5 initial rate (mol s ⁻¹)
5.7	70	2.77 ± 0.06
11.5	69	5.31 ± 0.12
23.1	70	10.05 ± 0.3

TABLE 2

KINETIC RESULTS FOR THE REACTION OF $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{COD})]$ WITH DMAD IN TOLUENE AT $109 \pm 0.1^\circ\text{C}$

$10^3[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{COD})]$ (mol dm ⁻³)	$10^2[\text{DMAD}]$ (mol dm ⁻³)	10^5 init. rate (mol s ⁻¹)	$10^3k^{\star a}$ (l mol ⁻¹ s ⁻¹)
4.05	44	0.31 ± 0.1	7.04
4.05	57	0.46 ± 0.2	8.07
4.05	70	0.60 ± 0.3	8.57
4.05	88	0.77 ± 0.4	8.75
4.05	99	0.85 ± 0.4	8.58

^a $k^{\star}$ refers to $k_{\text{obs}}/[\text{catalyst}]$.

order plots were obtained for up to at least 60% conversion, and in each case the first order relationship was obeyed throughout the entire kinetic run indicating that the catalyst concentration remained constant. Each kinetic run was carried out at least twice to check the reproducibility. From the results shown in Table 3 it can be seen that for the π -acceptor acetylene DMAD the rate of reaction increases in the order $[(\eta^5\text{-C}_5\text{Cl}_5)\text{Rh}(\text{COD})] < [(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{COD})] < [(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{COD})]$, while the opposite trend is apparent with the more electron-rich acetylene, hex-3-yne, although the observed rate differences are not very large. Attempts to carry out a similar series of reactions with the catalysts $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2]$, $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2]$ and $[(\eta^5\text{-C}_5\text{Cl}_5)\text{Rh}(\text{CO})_2]$ were less successful. The last complex proved to be very unstable and all attempts to isolate it have failed. As a substitute example of a rhodium dicarbonyl complex having a π -acceptor cyclopentadienyl ligand we investigated the use of the recently reported complex $[(\eta^5\text{-C}_5\text{H}_4\text{PPh}_3)\text{Rh}(\text{CO})_2]\text{PF}_6$ [14] as a catalyst. The reactions of the dicarbonyl complexes were not as well behaved kinetically as those of the cycloocta-1,5-diene derivatives. This is particularly true of the cyclotrimerization of DMAD using $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2]$. This reaction showed significant deviation from first order behaviour after only 20% conversion, and this is clearly seen in Fig. 2. The results did not fit any other simple order, and the same behaviour was not observed with hex-3-yne, suggesting that

TABLE 3

RATES OF CYCLOTRIMERIZATION OF DMAD AND HEX-3-YNE IN TOLUENE AT $109 \pm 0.1^\circ\text{C}$ WITH THE CATALYSTS $[\text{Rh}(\eta^5\text{-C}_5\text{X}_5)(\text{COD})]$ (X = Me, H, Cl)

Catalyst ^a	Acetylene ^b	10^5 init. rate (mol s ⁻¹)	10^5k_{obs} (s ⁻¹)	$10^3k^{\star c}$ (l mol ⁻¹ s ⁻¹)
$\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{COD})$	DMAD	2.31 ± 0.06	3.88 ± 0.09	6.80
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{COD})$	DMAD	1.78 ± 0.07	2.36 ± 0.12	4.14
$\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})$	DMAD	1.26 ± 0.08	1.28 ± 0.05	2.24
$\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{COD})$	EtC ₂ Et	1.80 ± 0.12	2.76 ± 0.10	4.84
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{COD})$	EtC ₂ Et	2.45 ± 0.08	3.83 ± 0.11	6.72
$\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})$	EtC ₂ Et	3.58 ± 0.10	4.30 ± 0.14	7.54

^a Catalyst concentration 5.7×10^{-3} mol dm⁻³. ^b Acetylene concentration 0.7 mol dm⁻³. ^c $k^{\star}$ refers to $k_{\text{obs}}/[\text{catalyst}]$.

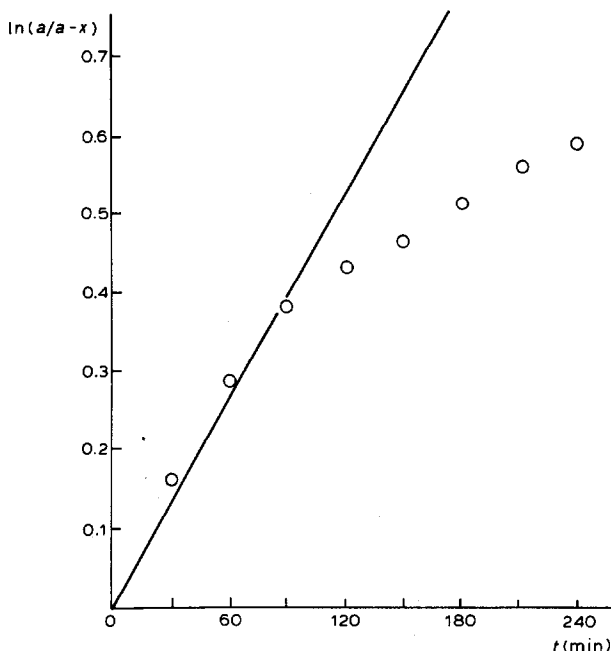


Fig. 2. Plot of $\ln(a/a-x)$ vs. time for the reaction of DMAD catalyzed by $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2]$.

DMAD may convert this complex into some catalytically inactive species during the reaction. From the results presented in Table 4 it can be seen that the rates of cyclotrimerization of DMAD are in the order $[(\eta^5\text{-C}_5\text{H}_5\text{PPh}_3)\text{Rh}(\text{CO})_2]\text{PF}_6 < [(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2] < [(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2]$, expected on the basis of the results obtained with the cycloocta-1,5-diene complexes, but the results with hex-3-yne are anomalous.

In an attempt to examine the effect of changing the ligand L the rates of cyclotrimerization of both DMAD and hex-3-yne have been determined for the complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhL}_2]$ ($\text{L} = \text{CO}, \text{C}_2\text{H}_4, \text{PF}_3$, and $\frac{1}{2}\text{COD}$). These reactions, with the exception of that between DMAD and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2]$ (vide supra),

TABLE 4

RATES OF CYCLOTRIMERIZATION OF DMAD AND HEX-3-YNE IN TOLUENE AT $109 \pm 0.1^\circ\text{C}$ WITH THE CATALYSTS $\text{Rh}(\eta^5\text{-C}_5\text{X}_5)(\text{CO})_2$ ($\text{X} = \text{Me}, \text{H}$) and $\text{Rh}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_3)(\text{CO})_2\text{PF}_6$

Catalyst ^a	Acetylene ^b	10^5 init. rate (mol s^{-1})	$10^5 k_{\text{obs}}$ (s^{-1})	$10^3 k^* c$ ($1 \text{ mol}^{-1} \text{ s}^{-1}$)
$\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2$	DMAD	3.38 ± 0.21	3.66 ± 0.21	6.42
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$	DMAD	2.03 ± 0.11	2.45 ± 0.09	4.29
$\text{Rh}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_3)(\text{CO})_2$	DMAD	1.55 ± 0.06	1.66 ± 0.07	2.91
$\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2$	EtC_2Et	3.41 ± 0.07	3.88 ± 0.22	6.80
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$	EtC_2Et	4.37 ± 0.08	5.43 ± 0.16	9.52
$\text{Rh}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_3)(\text{CO})_2$	EtC_2Et	2.83 ± 0.10	3.70 ± 0.13	6.49

^a Catalyst concentration $2.9 \times 10^{-3} \text{ mol dm}^{-3}$. ^b Acetylene concentration $0.352 \text{ mol dm}^{-3}$. ^c k^* refers to $k_{\text{obs}}/[\text{catalyst}]$.

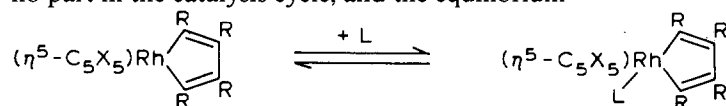
TABLE 5

RATES OF CYCLOTRIMERIZATION OF DMAD AND HEX-3-YNE IN TOLUENE AT $109 \pm 0.1^\circ\text{C}$ WITH THE CATALYSTS $\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{L}_2$ ($\text{L} = \text{C}_2\text{H}_4, \text{CO}, \text{PF}_3, \frac{1}{2}\text{COD}$)

Catalyst ^a	Acetylene ^b	10^5 init. rate (mol s^{-1})	$10^5 k_{\text{obs}}$ (s^{-1})	$10^3 k^* \text{ }^c$ ($\text{l mol}^{-1} \text{s}^{-1}$)
$\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_2\text{H}_4)_2$	DMAD	5.38 ± 0.07	8.33 ± 0.26	14.61
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{COD})$	DMAD	2.31 ± 0.06	3.88 ± 0.09	6.80
$\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2$	DMAD	3.38 ± 0.07	3.66 ± 0.21	6.42
$\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{PF}_3)_2$	DMAD	0.55 ± 0.03	0.30 ± 0.05	0.52
$\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_2\text{H}_4)_2$	EtC_2Et	1.70 ± 0.10	2.60 ± 0.12	4.56
$\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{COD})$	EtC_2Et	1.80 ± 0.12	2.76 ± 0.10	4.84
$\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2$	EtC_2Et	3.41 ± 0.07	3.88 ± 0.22	6.80
$\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{PF}_3)_2$	EtC_2Et	2.76 ± 0.06	2.90 ± 0.12	5.80

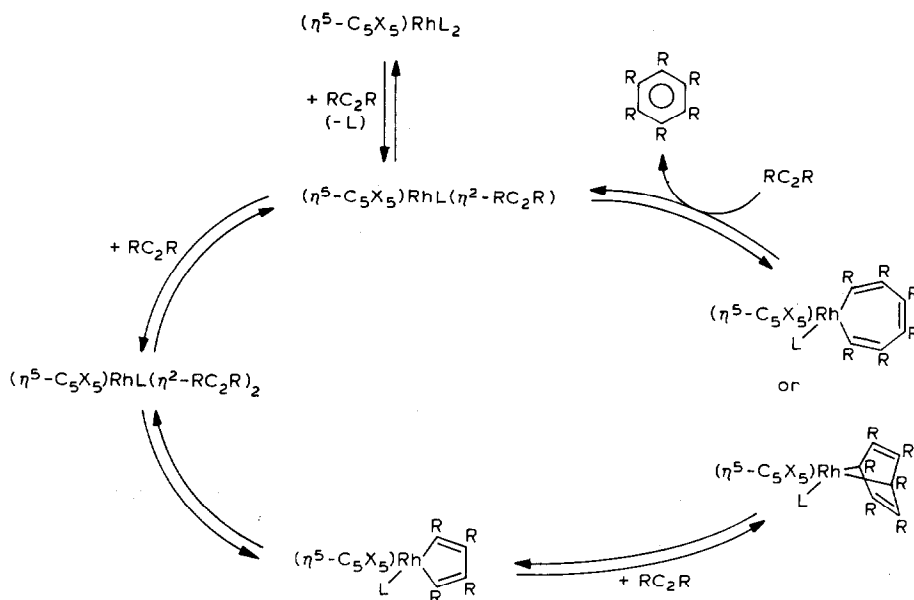
^a Catalyst concentration $2.9 \times 10^{-3} \text{ mol dm}^{-3}$. ^b Acetylene concentration $0.352 \text{ mol dm}^{-3}$. ^c k^* refers to $k_{\text{obs}}/[\text{catalyst}]$.

gave good first order plots up to at least 50% acetylene conversion, and the results are shown in Table 5. In all these reactions the $[\text{acetylene}]/[\text{catalyst}]$ mole ratio was 100/1, and thus the observed rates refer to the kinetics of the catalysis cycle only. The observed dependence of the rate of cyclotrimerization on the nature of the ligand L cannot be explained by a mechanism such as A (Scheme 1), since L plays no part in the catalysis cycle, and the equilibrium



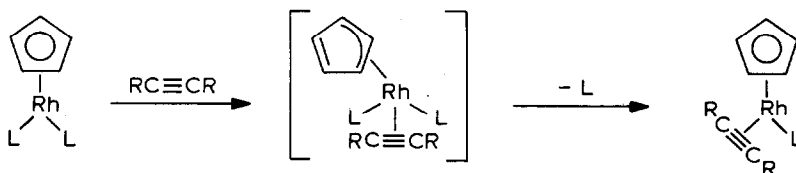
would be unimportant at the low catalyst concentrations employed. Clearly, in a mechanism such as B (Scheme 1) ligand L may influence the rate of cyclotrimerization provided that the conversion of the intermediate 1 to 2 ($\text{M} = \text{Rh}$) is rate-determining. However, this mechanism requires that L is lost during the catalysis cycle, and it is difficult to appreciate how such a mechanism could operate for more than one cycle when L is a volatile ligand such as CO , C_2H_4 or PF_3 especially at the reflux temperature of toluene. Separate experiments have shown that even when these rhodium-catalyzed reactions are carried out in the presence of added ligand L the reaction is not inhibited completely, although some inhibition is observed. So, for example, when the cyclotrimerization of DMAD was carried out using $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2]$ (acetylene/catalyst mole ratio 121/1) at the reflux temperature of toluene under 1 atm carbon monoxide the initial rate of reaction fell only from $3.38 \pm 0.07 \times 10^{-5} \text{ mol s}^{-1}$ to $2.03 \pm 0.20 \times 10^{-5} \text{ mol s}^{-1}$. Similarly, the cyclotrimerization of DMAD with $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{COD})]$ in the presence of free cycloocta-1,5-diene (mole ratio of catalyst/DMAD/COD of 1/121/121) caused the initial rate to drop from $2.31 \pm 0.06 \times 10^{-5} \text{ mol s}^{-1}$ to $1.26 \pm 0.04 \times 10^{-5} \text{ mol s}^{-1}$, and with a catalyst/DMAD/COD mole ratio of 1/121/242 the initial rate fell to $0.80 \pm 0.03 \times 10^{-5} \text{ mol s}^{-1}$.

While these results do not entirely eliminate mechanism B (Scheme 1), another possible explanation for the observations is that the ligand L stays on the rhodium atom throughout the catalysis cycle (Scheme 2). This mechanism is open to the objection that apparent '20-electron' intermediates are involved, but it has been



SCHEME 2

recognised for a number of years that ligand exchange in $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2]$ ($\text{M} = \text{Co}, \text{Rh}$) occurs by an associative mechanism in which an η^5 to η^3 slippage of the cyclopentadienyl ligand is thought to occur [15–18].



Rerek and Basolo [18] have shown that for substitution of carbon monoxide by the donor ligand, PPh_3 , electron-withdrawing substituents, such as NO_2 or PPh_3 , accelerate $\text{S}_{\text{N}}2$ substitution. Similar results were found by Cramer and Seiwel [16] when comparing the rates of substitution of an ethene ligand in $[\text{Rh}(\eta^5\text{-C}_5\text{H}_4\text{CN})(\text{C}_2\text{H}_4)_2]$ and $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4)_2]$. Conversely, electron-donating substituents on the cyclopentadienyl ring make the η^5 – η^3 “slippage” more difficult for attack by a donor ligand, but enhance reaction with an electrophilic ligand. These conclusions agree well with our observations that in the reactions with hex-3-yne the rates of cyclotrimerization are in the order $(\eta^5\text{-C}_5\text{Cl}_5) > (\eta^5\text{-C}_5\text{H}_5) > (\eta^5\text{-C}_5\text{Me}_5)$, while the reverse is true for the electrophile DMAD.

An important consequence of the mechanism outlined in Scheme 2 is that by changing the ligand L it should be possible to exert some control over the reaction. When L is a good donor ligand, e.g. C_2H_4 , COD , or PR_3 cyclotrimerization of an electron-deficient acetylene should be favoured, but the reverse will be true for acceptor ligands such as CO or PF_3 . This is supported by the kinetic results presented in Table 5 and the qualitative results described in Table 6. This may, of course, be an oversimplification especially in the case of the diolefin ligand COD . In their elegant study of cyclotrimerization reactions catalyzed by the η^5 -indenyl

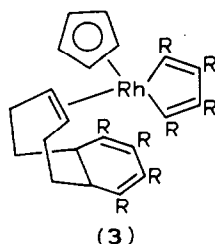
TABLE 6

SELECTIVE CYCLOTRIMERIZATION REACTIONS OF ACETYLENES USING η^5 -CYCLOPENTADIENYL- AND η^5 -INDENYL-RHODIUM CATALYSTS ^a

Catalyst	Acetylene	Solvent	Product (% yield) ^b
Rh(η^5 -C ₅ Me ₅)(COD)	DMAD	toluene	C ₆ (CO ₂ Me) ₆ (77)
Rh(η^5 -C ₅ Me ₅)(COD)	EtC ₂ Et	toluene	C ₆ Et ₆ (14)
Rh(η^5 -C ₅ Me ₅)(COD)	PhC ₂ Ph	xylene	C ₆ Ph ₆ (6)
Rh(η^5 -C ₅ Me ₅)(C ₂ H ₄) ₂	DMAD	toluene	C ₆ (CO ₂ Me) ₆ (77)
Rh(η^5 -C ₅ Me ₅)(C ₂ H ₄) ₂	EtC ₂ Et	toluene	C ₆ Et ₆ (22)
Rh(η^5 -C ₅ Me ₅)(C ₂ H ₄) ₂	PhC ₂ Ph	toluene	C ₆ Ph ₆ (62)
Rh(η^5 -C ₅ H ₅)(COD)	DMAD	toluene	C ₆ (CO ₂ Me) ₆ (74)
Rh(η^5 -C ₅ H ₅)(COD)	HC ₂ CO ₂ Et	toluene	1,3,5-C ₆ H ₃ (CO ₂ Et) ₃ (42) 1,2,4-C ₆ H ₃ (CO ₂ Et) ₃ (42)
Rh(η^5 -C ₅ H ₅)(COD)	PhC ₂ Ph	toluene	C ₆ Ph ₆ (< 1)
Rh(η^5 -C ₅ Cl ₅)(COD)	DMAD	toluene	C ₆ (CO ₂ Me) ₆ (39)
Rh(η^5 -C ₅ Cl ₅)(COD)	PhC ₂ Ph	xylene	C ₆ Ph ₆ (< 1)
Rh(η^5 -C ₅ Me ₅)(CO) ₂	DMAD	toluene	C ₆ (CO ₂ Me) ₆ (52)
Rh(η^5 -C ₅ Me ₅)(CO) ₂	PhC ₂ Ph	toluene	C ₆ Ph ₆ (34)
Rh(η^5 -C ₉ H ₇)(COD) ^c	DMAD	toluene	C ₆ (CO ₂ Me) ₆ (82)
Rh(η^5 -C ₉ H ₇)(COD) ^c	HC ₂ CO ₂ Et	toluene	1,3,5-C ₆ H ₃ (CO ₂ Et) ₃ (47) 1,2,4-C ₆ H ₃ (CO ₂ Et) ₃ (47)

^a Except where stated, reactions were carried out using 0.29 mmol catalyst and 35.18 mmol acetylene at the reflux temperature of the solvent for 24 h. ^b Yield of isolated product. ^c Using catalyst (0.144 mmol) and acetylene (17.5 mmol) at the reflux temperature of the solvent for 2 h.

complexes of the type [Rh(alkene)₂(η^5 -C₉H₇)] and [Rh(diene)(η^5 -C₉H₇)] Green and co-workers [19] have shown that formation of a rhodacyclopent-2-ene intermediate by coupling of an acetylene and an alkene ligand competes with the formation of the rhodacyclopentadiene intermediate. It is possible that the true catalysts in the cyclotrimerization reactions catalyzed by [(η^5 -C₅X₅)Rh(COD)] (X = H, Me, Cl) may be a complex such as **3** formed by coupling of one of the olefinic bonds of the COD ligand.



If so, the alkene ligand could exert a considerable steric as well as electronic influence upon the course of the reaction, and this may explain the differences in the rates of catalysis observed with [(η^5 -C₅Me₅)Rh(COD)] and [(η^5 -C₅Me₅)Rh(C₂H₄)₂] (Tables 5 and 6).

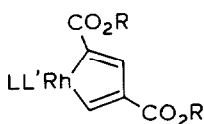
Preliminary experiments designed to investigate whether the nature of L can exert some control in co-oligomerization reactions have been carried out using mixtures of an electron-deficient and an electron-rich acetylene. In theory, co-oligomerization of two different acetylenes RC₂R and R'C₂R' can give four possible benzenes C₆R₆, C₆R'₆, C₆R₄R'₂, and C₆R₂R'₄ and previous work with [(η^5 -C₅H₅)Co(CO)₂] has shown that it is non-selective yielding the expected mixture of trimers, except when one of the acetylenes does not cyclotrimerize, e.g. Me₃SiC₂SiMe₃ [2]. For compari-

TABLE 7

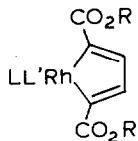
COMPARISON OF THE CO-CYCLOTTRIMERIZATION REACTIONS OF ACETYLENES WITH η^5 -CYCLOPENTADIENYL- AND INDENYL-RHODIUM COMPLEXES

Catalyst	Acetylenes (mol ratio)	Products (% yield)
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{COD})^a$	DMAD/ $\text{HC}_2\text{CMe}_2\text{OH}$ (2/1)	$\text{C}_6(\text{CO}_2\text{Me})_6$ (17) (A) (42)
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{COD})^a$	DMAD/ $\text{HC}_2\text{CMe}_2\text{OH}$ (4/1)	$\text{C}_6(\text{CO}_2\text{Me})_6$ (4) (A) ^d (32)
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4)_2^a$	DMAD/ EtC_2Et (1/1)	1,2- $\text{C}_6\text{Et}_2(\text{CO}_2\text{Me})_4$ (23) $\text{C}_6(\text{CO}_2\text{Me})_6$ (21)
$\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2^a$	DMAD/ PhC_2Ph (1/1)	1,2- $\text{C}_6\text{Ph}_2(\text{CO}_2\text{Me})_4$ (5) $\text{C}_6(\text{CO}_2\text{Me})_6$ (30)
$\text{Rh}(\eta^5\text{-C}_9\text{H}_7)(\text{COD})^b$	DMAD/ $\text{HC}_2\text{CMe}_2\text{OH}$ (2/1)	$\text{C}_6(\text{CO}_2\text{Me})_6$ (19) (A) ^d (57)
$\text{Rh}(\eta^5\text{-C}_9\text{H}_7)(\text{COD})^d$	DMAD/ EtC_2Et (2/1)	$\text{C}_6(\text{CO}_2\text{Me})_6$ (48) 1,2- $\text{C}_6\text{Et}_2(\text{CO}_2\text{Me})_4$ (36)
$\text{Rh}(\eta^5\text{-C}_9\text{H}_7)(\text{COD})^c$	$\text{HC}_2\text{CO}_2\text{Et}/\text{HC}_2\text{CMe}_2\text{OH}$ (2/1)	(B) ^e (83)

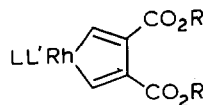
^a Acetylene/catalyst molar ratio 121/1 in refluxing toluene (10 cm³) for 24 h. ^b Acetylene/catalyst molar ratio 121/1 in refluxing toluene (10 cm³) for 2 h. ^c Addition of $\text{HC}_2\text{CO}_2\text{Et}$ (7.0 mmol) dropwise over 2 h to a solution of $\text{HC}_2\text{CMe}_2\text{OH}$ (3.5 mmol) and $\text{Rh}(\eta^5\text{-C}_9\text{H}_7)(\text{COD})$ (0.87 mmol) in refluxing toluene (10 cm³).



(4)



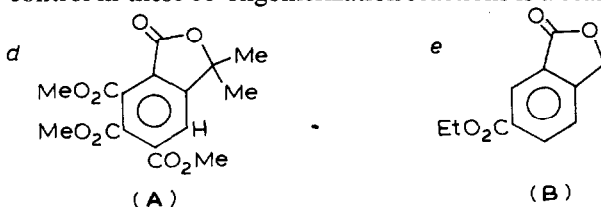
(5)



(6)

son purposes we have also studied the selectivity of the η^5 -indenyl complex [$(\eta^5\text{-C}_9\text{H}_7)\text{Rh}(\text{COD})$] under similar conditions. As Green [19] has noted previously the η^5 -indenyl ligand undergoes a facile slippage to an η^3 -indenyl ligand, and should catalyze cyclotrimerization reactions by a similar mechanism to that proposed for the η^5 -cyclopentadienylrhodium complex. Under pseudo-first-order conditions (acetylene/ $(\eta^5\text{-C}_9\text{H}_7)\text{Rh}(\text{COD})$ mole ratio 121/1) the cyclotrimerization of DMAD in refluxing toluene gave a good straight-line plot of $\ln(a/a-x)$ vs. time for at least 85% conversion, and the initial reaction rate (averaged over three kinetic runs) was found to be $1.91 \times 10^{-4} \text{ mol s}^{-1}$, i.e. approximately ten times faster than the corresponding reaction catalyzed by $(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{COD})$. Reaction was complete after only 2 h to give an 85% isolated yield of hexacarbomethoxybenzene, and there was no polymeric red gum usually formed as a by-product in reactions involving prolonged heating of DMAD. This enhanced activity caused by the more facile η^5 to η^3 slippage agrees with the findings of Green and co-workers. The comparative results of the cyclotrimerization reactions are presented in Table 7. It can be seen from the results that the two catalysts have similar selectivities, although the indenyl complex gives cleaner product mixtures in much shorter reaction times resulting in slightly higher product yields. The unsymmetrical acetylene, ethyl propiolate, gave an approximate equimolar mixture of the two possible products implying that only the sterically least hindered 2,4-rhodacycle intermediates 4 ($\text{L} = \eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_9\text{H}_7$; $\text{L}' = \text{COD}$ or $\text{COD}:2\text{RC}_2\text{H}$ adduct) are involved in the catalysis cycles. This

conclusion is supported by the formation of a single lactone product from the co-oligomerization of $\text{HC}_2\text{CO}_2\text{Et}$ and $\text{HC}_2\text{CMe}_2\text{OH}$, neither of the alternative rhodacycle intermediates **5** or **6** could give rise to this product. Similar conclusions were reached by Green to explain the ratio of tri(*t*-butyl)benzenes and tri(carboethoxy)benzenes from HC_2Bu^t and $\text{HC}_2\text{CO}_2\text{Et}$ respectively [19]. The observed selectivity in these preliminary experiments is encouraging and suggests that product control in these co-oligomerization reactions is a real possibility.



Experimental

The complexes $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ [20], $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{COD})]$ [21,22], $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$ [22], $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_2\text{H}_4)_2]$ [23], $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{PF}_3)_2]$ [24], $[\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})]$ [25] and $[\text{Rh}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_3)(\text{CO})_2]\text{PF}_6$ [14] were prepared by previously reported procedures. The complex $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{COD})]$ (m.p. 166–167°C) was prepared in 89% yield by heating a mixture of $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$ [26], cycloocta-1,5-diene and sodium carbonate in dry ethanol under reflux for 2 h.

Liquid acetylenes were purified by distillation under an atmosphere of dry nitrogen and the purity (>99%) was checked by GLC. Solid acetylenes were recrystallised to constant m.p. All solvents were dried and purified by standard procedures [27]. New compounds were characterised by IR spectroscopy (Perkin–Elmer 735), NMR spectroscopy (Perkin–Elmer R32 (90 MHz) or R34 (220 MHz) for ^1H), and mass spectrometry (AEI MS 45 operating at an ionising electron beam energy of 70 eV). Except where stated, reactions were carried out under nitrogen dried by passage through a tube packed with P_2O_5 and de-oxygenated by passing over a heated copper oxide catalyst at 200°C.

Preparation of $[\text{Rh}(\eta^5\text{-C}_9\text{H}_7)(\text{COD})]$

A solution of sodium indenide (1 mmol) in tetrahydrofuran was added to a suspension of bis[chloro(cycloocta-1,5-diene)rhodium] (0.49 g, 1 mmol) in tetrahydrofuran (10 cm^3), and the mixture was stirred for 18 h at room temperature. Removal of the solvent gave a brown gum which was extracted with diethyl ether (3 $\times$ 5 cm^3) and the extract was concentrated and chromatographed (Florisil; ether eluant) to give yellow needles of $[\text{Rh}(\eta^5\text{-C}_9\text{H}_7)(\text{COD})]$ (0.07 g, 0.22 mmol, 22%) m.p. 100–101°C [^1H NMR (CDCl_3 ; Me_4Si reference): δ 1.75 (br m, 8H, CH_2 of COD ligand), 3.95 (m, 4H, $\text{CH}=\text{CH}$ of COD ligand), 5.12 (m, 2H), 6.05 (m, 1H, $J(\text{H}-\text{H})$ 3, $J(\text{Rh}-\text{H})$ 1 Hz) and 7.3–6.9 (m, 4H); MS (FAB technique [28]) m/z 326 [M] $^+$, 296 [$(\text{C}_9\text{H}_7)\text{Rh}(\text{C}_6\text{H}_6)$] $^+$, 218 [$(\text{C}_9\text{H}_7)\text{Rh}$] $^+$, 205 [$(\text{C}_8\text{H}_6)\text{Rh}$] $^+$, 181 [$(\text{C}_6\text{H}_6)\text{Rh}$] $^+$, 115 [RhCl] $^+$].

Co-oligomerization reactions catalyzed by $[\text{Rh}(\eta^5\text{-C}_9\text{H}_7)(\text{COD})]$ and $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{COD})]$

In a typical reaction the catalyst (0.01 g) was added to a solution of the two acetylenes (3.5 mmol each) in toluene (10 cm^3) and the mixture was heated under

reflux for 2 h. The solvent was removed under vacuum and the residue was examined by thin-layer chromatography. Where only one product was obtained, this was usually recrystallised from a mixture of dichloromethane and ether (1/1). Mixed products were separated by chromatography (Florisil; CH_2Cl_2 /ether (1/1) eluant).

Hexacarbomethoxybenzene, 1,3,5- and 1,2,4-tricarbomethoxybenzene were identified by comparison of their IR and ^1H NMR spectra with those of authentic samples. The phthalide (A), m.p. 162°C was identified from the following data [IR (Nujol mull) $\nu(\text{C}=\text{O})$ 1730 and 1780 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.70 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 4.12 (s, 9H, OCH_3), and 8.19 (s, 1H, aromatic); MS m/z 336 $[M]^+$ 1.2%, 321 $[M - \text{CH}_3]^+$ 100%, 293 $[M - \text{CH}_3 - \text{CO}]^+$ 26%, 101 $[\text{C}_1\text{HO}]_4^+$ 12%, 73 $[\text{C}_6\text{H}]^+$ 7%. The phthalide B, m.p. $64\text{--}67^\circ\text{C}$, was identified from the following data [IR (Nujol mull) $\nu(\text{C}=\text{O})$ 1730 and 1780 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.40 (t, 3H, J 7 Hz, CH_3), 1.70 (s, 6H, CH_3), 4.45 (q, 2H, OCH_2), 7.92 (d, 1H, J 8 Hz), 8.08 (d, 1H, J 2 Hz) and 8.18 (dd, 1H); MS m/z 234 $[M]^+$ 1.9%, 219 $[M - \text{CH}_3]^+$ 100%, 191 $[M - \text{CH}_3 - \text{CO}]^+$ 31.2%, 103 $[\text{C}_7\text{H}_3\text{O}]$ 15.7%, 75 $[\text{C}_6\text{H}_3]$ 11.3%.

Kinetic studies

Reactions were monitored by GLC (Pye-Unicam 104 with flame ionisation detector; 1.2m OV1 column; Hewlett-Packard 3352B integrator) using dimethyldigol as internal standard. The accuracy and reproducibility of the GLC analyses were checked by injecting six standard solutions of DMAD and dimethyldigol (mole ratios 2.5–0.25/1) in toluene, and five standard solutions of hex-3-yne and dimethyldigol (mole ratios 1.0–0.25/1) in toluene. Plots of peak area vs. [acetylene] were linear and reproducible in all cases.

In a typical reaction dimethyldigol (4.72 g, 35.17 mmol), the acetylene (35.18 mmol) and toluene (41.5 cm^3) were injected into a flame-dried, three-necked flask (250 cm^3) fitted with a reflux condenser and containing an atmosphere of dry nitrogen. The mixture was heated with stirring in a thermostatted Lissapol bath at $113 \pm 1^\circ\text{C}$ and the catalyst (0.29 mmol) in toluene was then injected. Samples (0.1 μl) were taken at 30 min intervals and the acetylene concentration was calculated in each case from the ratios of the areas of dimethyldigol/acetylene. The standard deviation calculated for the initial rate of reaction from the plots of [acetylene] vs. time was found to be in the region of 1.2–6%, and in the majority of cases the error was below 4%. The standard error in the first order plots of $\ln(a/a - x)$ versus time was obtained by the method of least mean squares (Hewlett-Packard 9800 computer), and was found to be in the range 2–4%.

References

- 1 Y. Wakatsuki and H. Yamazaki, *Tetrahedron Letters*, (1973) 3385; *Synthesis*, (1976) 26; *J. Organomet. Chem.*, 139 (1977) 157, 169; *J. Chem. Soc., Dalton Trans.*, (1978) 1278; *J. Am. Chem. Soc.*, 101 (1979) 1223.
- 2 K.P.C. Vollhardt, *Acc. Chem. Res.*, 10 (1977) 1; R.L. Funk and K.P.C. Vollhardt, *Chem. Soc. Rev.*, 9 (1980) 41; R.L. Hillard and K.P.C. Vollhardt, *Tetrahedron*, 36 (1980) 2435; K.P.C. Vollhardt, *Angew. Chem. Int. Ed. Engl.*, 23 (1984) 539.
- 3 W.S. Lee and H.H. Brintzinger, *J. Organomet. Chem.*, 127 (1977) 93.
- 4 G. Gubitosi, M. Boldt, and H.H. Brintzinger, *J. Amer. Chem. Soc.*, 99 (1977) 5174.
- 5 P. Hona and H. Yamazaki, *Tetrahedron Letters*, (1977) 1333.
- 6 D.R. McAllister, J.E. Bercaw, and R.G. Bergman, *J. Amer. Chem. Soc.*, 99 (1977) 1666.

- 7 L.P.M. Bushnell, E.R. Evitt, and R.G. Bergman, *J. Organomet. Chem.*, 157 (1978) 445.
- 8 R.S. Dickson and H.P. Kirsch, *Aust. J. Chem.*, 25 (1972) 2535; R.S. Dickson and L.J. Michel, *Aust. J. Chem.*, 28 (1975) 285.
- 9 S.A. Gardener, P.S. Andrews and M.D. Rausch, *Inorg. Chem.*, 12 (1973) 2396.
- 10 R.B. King and M.N. Ackermann, *J. Organomet. Chem.*, 67 (1974) 431.
- 11 M.D. Rausch and S.A. Gardener, *J. Organomet. Chem.*, 56 (1973) 365.
- 12 Y. Wakatsuki and H. Yamazaki, *J. Organomet. Chem.*, 64 (1974) 393.
- 13 R.G. Gastinger, M.D. Rausch, D.A. Sullivan, and G.J. Pallenik, *J. Organomet. Chem.*, 117 (1976) 355.
- 14 G. Tresoldi, A. Recca, P. Finocchiaro, and F. Faraone, *Inorg. Chem.*, 20 (1981) 3103.
- 15 A. Wojcicki and F. Basolo, *J. Inorg. Nucl. Chem.*, 17 (1961) 77; H.G. Schuster-Woldan and F. Basolo, *J. Amer. Chem. Soc.*, 88 (1966) 1657.
- 16 R. Cramer and L.P. Seiwel, *J. Organomet. Chem.*, 92 (1975) 245.
- 17 M.E. Rerek and F. Basolo, *Organometallics*, 2 (1983) 372; M.E. Rerek, L.N. Ji and F. Basolo, *J. Chem. Soc., Chem. Commun.*, (1983) 1208.
- 18 M.E. Rerek and F. Basolo, *J. Amer. Chem. Soc.*, 106 (1984) 5908.
- 19 P. Caddy, M. Green, E. O'Brien, L.E. Smart, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, (1980) 962.
- 20 R.S. Dickson and G.R. Tailby, *Aust. J. Chem.*, 23 (1970) 1531.
- 21 J. Chatt and L. Venanzi, *J. Chem. Soc.*, (1957) 4735.
- 22 J.W. Kang and P.M. Maitlis, *J. Organomet. Chem.*, 26 (1971) 393.
- 23 K. Moseley, J.W. Kang and P.M. Maitlis, *J. Chem. Soc. (A)*, (1970) 2875.
- 24 R.B. King and A. Efraty, *J. Amer. Chem. Soc.*, 93 (1971) 5269.
- 25 K.J. Reimer and A. Shaver, *Inorg. Chem.*, 14 (1975) 2707.
- 26 B.L. Booth, R.N. Haszeldine and M. Hill, *J. Chem. Soc. (A)*, (1969) 1299.
- 27 H.J.E. Loewenthal, *Guide for the Perplexed Organic Experimentalist*, Heyden, 1978, p. 48-52.
- 28 M. Barber, R.S. Bordoli, R.D. Sedgwick, and A.N. Tyler, *Nature*, 293 (1981) 270.