

The photochemical generation of novel neutral mononuclear ruthenium complexes and their reactivity

Andrew J. Edwards^{*}, Nicholas E. Leadbeater, Jack Lewis, Paul R. Raithby^{*}

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

Received 30 August 1994

Abstract

The room-temperature photolysis of $\text{Ru}_3(\text{CO})_{12}$ (**1**) in dichloromethane under a flow of ethylene affords the highly reactive complex $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ (**2**) in a quantitative yield. The addition of MeCN to the reaction mixture, while the photolytic conditions and the ethylene flow are maintained, gives $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)(\text{NCMe})$ (**3**). If the irradiation is continued but the ethylene flow stopped, a different product, namely $\text{Ru}(\text{CO})_3(\text{NCMe})_2$ (**4**) is obtained. The addition of an excess of triphenylphosphine to a dichloromethane solution of **2** in the absence of ethylene and of light gives two phosphine-substituted products: $\text{Ru}(\text{CO})_4(\text{PPh}_3)$ (**5**) and $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**6**). Under similar conditions, **3** affords **6** and the trinuclear cluster $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ (**7**) while, if MeCN is added instead of PPh_3 , the reactive cluster $\text{Ru}_3(\text{CO})_9(\text{NCMe})_3$ (**8**) is obtained. If an excess of acrylonitrile is used instead of ethylene, the photolysis of **1** in dichloromethane yields $\text{Ru}(\text{CO})_4(\text{NCCH}=\text{CH}_2)$ (**9**) which reacts under photolytic conditions but in the absence of an excess of acrylonitrile with MeCN to give $\text{Ru}(\text{CO})_3(\text{NCCH}=\text{CH}_2)(\text{MeCN})$ (**10**) and this product reacts with a second equivalent of acrylonitrile to afford $\text{Ru}(\text{CO})_3(\text{NCCH}=\text{CH}_2)_2$ (**11**). All the products have been characterized by IR spectroscopy and their structures established from symmetry considerations.

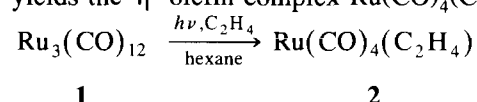
Keywords: Ruthenium; Carbonyl; Nitrile; Ethylene; Photochemical synthesis

1. Introduction

The majority of the routes to ruthenium cluster complexes involve either high temperatures and pressures or complicated, low yield methods that result in mixed products. Here we report a new route which involves the photochemical generation and subsequent reactions of mononuclear ruthenium complexes, and an investigation of the possibility of developing a versatile mononuclear ruthenium capping fragment that might be used to prepare target ruthenium-containing clusters simply and in a high yield.

Mononuclear ruthenium complexes may be generated from higher nuclearity compounds, in particular $\text{Ru}_3(\text{CO})_{12}$ (**1**) by a number of routes, of which the most selective involves a photochemical procedure. In 1974, Lewis and coworkers [1] reported that photolysis of a

solution of $\text{Ru}_3(\text{CO})_{12}$ (**1**) in hexane under ethylene yields the η^2 -olefin complex $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ (**2**):



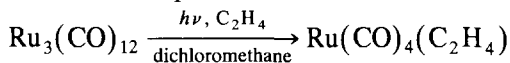
It has more recently been shown, first by Bruce and Stone [2] and later by Keister and coworkers [3], that the η^2 -ethylene complex **2** has great potential as a capping agent for a wide variety of species, essentially owing to the ease of loss of the olefin group to yield the reactive intermediate " $\text{Ru}(\text{CO})_4$ ". Such a method was used, for example, in the preparation of tetra-ruthenium systems such as $\text{HRu}_4(\text{CO})_{12}(\mu_4\text{-}\eta^2\text{-COMe})$ from triruthenium clusters [2].

To date, only relatively low concentrations of the ethylene complex have been observed on irradiation ($\lambda \approx 397$ nm) of a hexane solution of $\text{Ru}_3(\text{CO})_{12}$ (**1**) in the presence of ethylene. The use of hexane as a solvent also limits the number of potential clusters with which the mononuclear complex can react, because of poor solvation of both the high nuclearity clusters and the charged species.

^{*} Corresponding authors.

2. Results and discussion

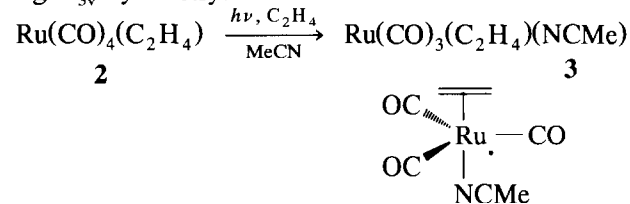
The ethylene complex $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ (**2**) can be prepared in a quantitative yield, and in a high concentration, from $\text{Ru}_3(\text{CO})_{12}$ (**1**) by using dichloromethane as the solvent in place of hexane:



The mononuclear complex **1** is stable in solution in the absence of light for a considerably longer time than in hexane. Hence, dichloromethane is potentially a better solvent for the photolysis, since high concentrations of the mononuclear complex **2** can be obtained. In addition this solvent system offers greater flexibility in the number of potential clusters that are soluble and hence available for reaction with the olefin complex generated. Despite these advantages, once the mononuclear is formed, the lability of its olefin ligand leads to ready trimerization back to the starting material **1**. In many cases the occurrence of this reaction also limits the practical utility of the mononuclear complex **2** as a capping fragment, as well as restricting the use of analytical techniques such as mass and NMR spectroscopy in the characterization of the mononuclear complex.

To circumvent the problem of regeneration of **1** we amended the synthesis to generate “ $\text{Ru}(\text{CO})_3$ ”-type precursors that are less likely to trimerize to **1**. Recent reports [4] have highlighted the catalytic behaviour of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ and other bis-phosphine complexes in the addition reactions of aromatic carbon–hydrogen bonds to olefins. This, in addition to knowledge of uses of such complexes in the hydroformylation and hydrogenation of olefins [5], prompted us to develop simple high yield routes to these complexes in addition to other bis disubstituted compounds that might show catalytic activity.

Previous photochemical studies [6] have shown that, following unimolecular dissociation of CO to form a coordinatively unsaturated intermediate, there is the opportunity for the carbonyl complexes to react with donor solvents to form weakly solvated species. If acetonitrile is added to a dichloromethane solution of **2** and irradiation continued, a new colourless complex is formed that shows two bands in the carbonyl region of the IR spectrum (Table 1). By application of Bor's [7] method of local symmetry, the product can be identified as the bis diaxial $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)(\text{MeCN})$ (**3**) possessing C_{3v} symmetry:



Again the lability of the ethylene and acetonitrile ligands precludes the use of other analytical techniques in the characterization of this complex.

In the pentacoordinate ethylene–acetonitrile complex, owing to the balance between σ and π interactions with the metal centre, the acetonitrile ligand will favour an axial site in the trigonal bipyramid. To reach the diaxial arrangement proposed, a rearrangement of the ethylene group is required from an equatorial position, as reported by Lewis and coworkers [1] for **2**, to a less favourable axial site. This is consistent with IR spectroscopic monitoring of the system on the addition of acetonitrile to the dichloromethane solution of **2**, which indicates the formation of a transient intermediate. This result is of importance since it appears to be the first report of a mononuclear ruthenium complex with an olefin in an axial position.

If the flow of ethylene through a solution of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)(\text{MeCN})$ (**3**) is stopped but irradiation

Table 1
Spectroscopic data for the new complexes

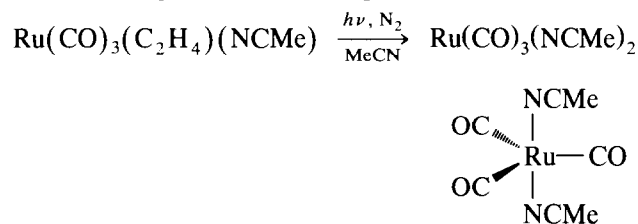
Compound	IR spectral data $\nu(\text{CO})$ (cm^{-1})	NMR spectral data ^a δ (ppm)
$\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ (2)	2015 (m), 2023 (vs), 1987 (s) ^b	
$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)(\text{NCMe})$ (3)	1995 (s), 1930 (vs) ^c	
$\text{Ru}(\text{CO})_3(\text{NCMe})_2$ (4)	1956 (vs) ^c	
$\text{Ru}(\text{CO})_4(\text{PPh}_3)$ (5)	2061 (s), 1987 (m), 1955 (vs) ^b	
$\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (6)	1895 (vs) ^b	
$\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ (7)	2044 (m), 1969 (vs) ^b	¹ H NMR: 7.43 (m) ³¹ P{ ¹ H} NMR: 103.7 (s)
$\text{Ru}_3(\text{CO})_9(\text{CNMe})_3$ (8)	2039 (m), 1967 (vs) ^c	¹ H NMR: 2.48 (s)
$\text{Ru}(\text{CO})_4(\text{NCC}=\text{CH}_2)$ (9)	2127 (m), 2051 (vs), 2017 (s), 1991 (m) ^b	¹ H NMR: 5.17 (s)
$\text{Ru}(\text{CO})_3(\text{NCH}=\text{CH}_2)(\text{NCMe})$ (10)	2069 (s), 1989 (vs) ^c	¹ H NMR: 2.17 (s), 2.74 (s), 5.44 (s)
$\text{Ru}(\text{CO})_3(\text{NCH}=\text{CH}_2)_2$ (11)	1947 (vs) ^c	¹ H NMR: 2.24 (s), 2.85 (s)

^a For the ³¹P NMR spectra all chemical shifts are relative to $\text{P}(\text{OMe})_3$ and for ¹H NMR spectra the solvent resonance was used as reference. All spectra were recorded with CDCl_3 as the solvent.

^b CH_2Cl_2 solvent.

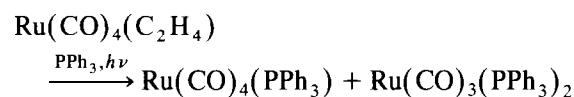
^c MeCN solvent.

continued, a further new colourless mononuclear complex is formed that has one IR absorption in the carbonyl region (Table 1). This is consistent with a D_{3h} $\text{Ru}(\text{CO})_3(\text{MeCN})_2$ (**4**) species, suggesting direct substitution of the ethylene group by a second acetonitrile molecule to give a bis diaxial product:

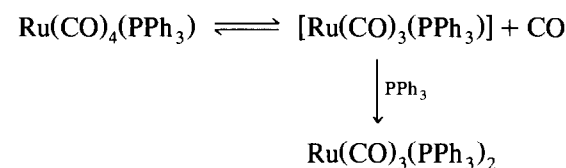


It is known that phosphines will replace labile ligands in mononuclear complexes to form simple substitution products [8]. Comparison of the IR data recorded (Table 1) for products with those available for the large number of phosphine complexes in the literature allows simple product characterization. For this reason the structure and reactions of the mononuclear species generated in the photochemistry of triruthenium dodecacarbonyl were further investigated by examining substitution by simple phosphines.

Addition of an excess of triphenylphosphine to a solution of **2** in dichloromethane in the absence of ethylene and light leads to the formation of an approximate 2 : 1 ratio (as judged from IR data) of the mono- to bis-triphenylphosphine-substituted products $\text{Ru}(\text{CO})_4(\text{PPh}_3)$ (**5**) and $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**6**) which is in agreement with reported data [1,9]:

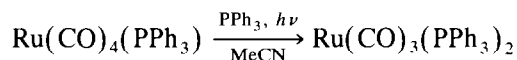


The IR spectra of the two products (Table 1) points to a C_{3v} arrangement in the monosubstituted product **5**, with the phosphine group in an axial position, and D_{3h} symmetry for the bis product **6**, with the two phosphine groups occupying the axial positions. Since the ethylene group on the η^2 -olefin complex **2** is in an equatorial position, the formation of the monosubstituted phosphine complex **5** with concomitant migration of the phosphine from an equatorial to an axial position may be postulated. The formation of the bis-substituted phosphine **6** from the monosubstituted species may be rationalized in terms of the dissociative mechanism involving the replacement of a carbonyl ligand by a further phosphine molecule [10]:



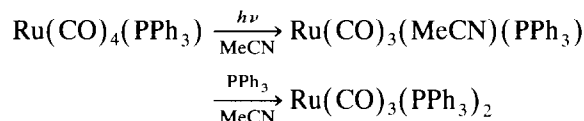
Addition of acetonitrile to the mixture of monosubsti-

tuted and bis-substituted phosphines still under irradiation leads to formation of the bis-phosphine product **6** in quantitative yield, as indicated by IR spectroscopy (Table 1):

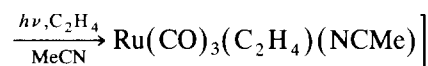


This reaction is performed at room temperature or below and provides a novel high yield route to bis-substituted phosphines whereas high temperatures and pressures or complicated procedures were previously required to obtain reasonable yields.

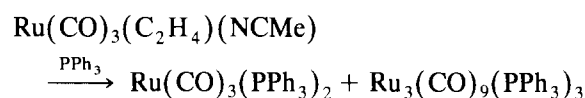
As indicated earlier, such a route is of particular importance because of the reported catalytic activity of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$. More importantly, the quantitative formation of the bis-phosphine product **6** on addition of acetonitrile to an irradiated solution of the monosubstituted phosphine product in dichloromethane points to replacement of a carbonyl group by an acetonitrile ligand which, in turn, is replaced by triphenylphosphine. This provides further evidence for the formation of an ethylene-acetonitrile intermediate $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)(\text{NCMe})$ (**3**) on addition of acetonitrile to an irradiated dichloromethane solution of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ (**2**):



[cf. $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$



In an attempt to throw further light on the structure and reactivity of the mononuclear intermediate **3** in acetonitrile, this complex was treated with triphenylphosphine in the absence of light. The reaction gave a mixture of two products $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**6**) and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ (**7**) in approximately equivalent amounts, and no monosubstituted product was observed:



7

The acetonitrile-containing mononuclear intermediates **3** and **4** are only stable under constant irradiation, because of the ready formation of higher nuclearity products. If the light source is removed at a low temperature, a new trinuclear ruthenium intermediate is formed. The symmetry of the IR spectrum (Table 1) and the $\nu(\text{CO})$ stretching frequencies for this intermediate are very similar to that of the previously described complex **7**.

It may be postulated that trimerization occurs with the loss of ethylene in the case of **3** and of acetonitrile

symmetry, and hence the same number of bands in the IR spectrum. Since a change from three bands to one is observed, we conclude that a diaxial arrangement in both complexes is most probable.

3. Experimental details

Unless otherwise stated all reactions were performed under dry nitrogen using standard Schlenk techniques. Solvents were distilled prior to use. Published methods were used to prepare the starting material $\text{Ru}_3(\text{CO})_{12}$ [2].

All photochemical reactions were performed in a glass vessel fitted with a gas bubbler, reflux condenser and a dry-ice cooling finger which was used to keep the reaction mixture at the required temperature. A 100 W lamp was used as the light source.

Routine separation of products was performed by thin layer chromatography (TLC), usually on commercially prepared glass plates, pre-coated to a thickness of 0.25 mm with Merck Kieselgel 60 F_{254} as supplied by Merck. Alternatively laboratory-prepared glass plates, coated to a thickness of 1.0 mm with Merck Kieselgel 60 F_{254} , were used.

IR spectra were recorded with a Perkin–Elmer 1710 Fourier transform IR spectrometer. NMR spectra were recorded with a Bruker AM400, WM250 or WP80SY Fourier transform NMR spectrometer. Mass spectra were recorded using an AEI MS 902 instrument.

3.1. Photochemical generation of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ (**2**) in dichloromethane

A dichloromethane solution of $\text{Ru}_3(\text{CO})_{12}$ (100 mg) was irradiated, and a flow of ethylene was kept throughout the time of exposure. The solution was maintained at below 10°C by means of the cooling finger. The solution became colourless after approximately 3 h, indicating the presence of the mononuclear species (yield, quantitative by IR), IR (CH_2Cl_2): $\nu(\text{CC})$ 2105(m), 2023(vs), 1987(s) cm^{-1} .

3.2. Reaction of **2** with acetonitrile under photochemical conditions and in the presence of a flow of ethylene

A dichloromethane solution of $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ (200 mg) was reduced to a small volume, acetonitrile (150 ml) was added, and the solution was irradiated and maintained below 10°C. A flow of ethylene through the solution was maintained throughout. A change in IR spectrum occurred but the solution remained colourless suggesting that the product was mononuclear. The reaction was characterized as $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)(\text{NCMe})$ (**3**) (yield, quantitative by IR). IR (acetonitrile): $\nu(\text{CO})$ 1995(s), 1930(vs) cm^{-1} .

3.3. Reaction of $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)(\text{NCMe})$ (**3**) with acetonitrile under photochemical conditions and in the absence of a flow of ethylene

An acetonitrile solution of **3** (200 mg) was irradiated while maintained below 10°C. A colourless mononuclear complex was generated and identified as $\text{Ru}(\text{CO})_3(\text{NCMe})_2$ (**4**) (yield, quantitative by IR). IR (MeCN): $\nu(\text{CO})$ 1956(vs) cm^{-1} .

3.4. Reaction of **2** with PPh_3

An excess of triphenylphosphine (60 mg) was added to a solution of **2** (100 mg) in dichloromethane and the mixture stirred for 1 h. The product was an approximate 2 : 1 ratio of mono-to-bis-triphenylphosphine-substituted species, $\text{Ru}(\text{CO})_4(\text{PPh}_3)$ (**5**) and $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**6**). IR (CH_2Cl_2): $\nu(\text{CO})$ mono 2061(s), 1987(m), 1955(vs); bis 1895 cm^{-1} . Anal. Mono found: C, 55.31; H, 3.14; P, 6.60. $\text{C}_{22}\text{H}_{15}\text{O}_4\text{PRu}$ calc.: C, 55.58; H, 3.18; P, 6.52. bis found: C, 65.39, H, 4.39, P, 8.75. $\text{C}_{39}\text{H}_{30}\text{O}_3\text{P}_2\text{Ru}$ calc.: C, 66.01; H, 4.26; P, 8.85%. Mass spectrum: m/z mono 475; bis 709.

3.5. Reaction of **3** with PPh_3

An excess of triphenylphosphine (50 mg) was added to a cooled solution of **3** (150 mg) in acetonitrile. The mixture was stirred rapidly, forming a deep-red solution. After 30 min the solvent was reduced under vacuum and the deep-red solution subjected to TLC (50 : 50 dichloromethane: hexane–silica) to give $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ (**6**) and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ (**7**) in a 1 : 1 ratio. IR (CH_2Cl_2) $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$: $\nu(\text{CO})$ 2044(m), 1969(vs) cm^{-1} . ^1H NMR(CDCl_3): δ 7.43(m) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR(CDCl_3): δ –103.7 (s) ppm. Anal. Found: C, 56.15, H, 3.31, P, 6.79. $\text{C}_{63}\text{H}_{45}\text{O}_9\text{P}_3\text{Ru}_3$ calc.: C, 56.29, H, 3.37; P 6.91%. Mass spectrum: m/z 1341. IR (CH_2Cl_2) $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$: $\nu(\text{CO})$ 1895 cm^{-1} .

3.6. Synthesis of $\text{Ru}_3(\text{CO})_9(\text{CNMe})_3$ (**8**)

An irradiated solution of **3** was kept below 10°C and the solution saturated with nitrogen. The solution was kept below 10°C for 30 min, and the reaction vessel was then sealed and the light source removed. Rapid formation of the trinuclear tris-acetonitrile complex $\text{Ru}_3(\text{CO})_9(\text{CNMe})_3$ (**10**) was observed (yield, quantitative by IR). IR (CH_2Cl_2): $\nu(\text{CO})$ 2039(m), 1967(vs) cm^{-1} . ^1H NMR(CDCl_3): δ 2.48(s) ppm.

3.7. Photochemical generation of $\text{Ru}(\text{CO})_4(\text{NCCH}=\text{CH}_2)$, **9**, in dichloromethane

A dichloromethane solution of $\text{Ru}_3(\text{CO})_{12}$ (100 mg) and an excess of acrylonitrile (20 ml) was irradiated

with a flow of nitrogen maintained throughout. A colourless solution was formed, indicating the formation of a mononuclear species (yield, quantitative by IR). IR (CH_2Cl_2): $\nu(\text{CO})$ 2127(m), 2051(vs), 2017(s), 1991(m) cm^{-1} . $^1\text{H NMR}$ (CDCl_3): δ 5.17(s) ppm.

3.8. Reaction of **9** with acetonitrile under irradiation

A dichloromethane solution of **9** (100 mg) was reduced to a small volume; then acetonitrile (150 ml) was added and the mixture was irradiated while kept below 10°C . A flow of nitrogen was maintained throughout. Comparison of the IR spectrum of the product with that of **3** indicated that the acrylonitrile–acetonitrile complex $\text{Ru}(\text{CO})_3(\text{NCCH}=\text{CH}_2)(\text{NCMe})$ (**10**) was formed (yield, quantitative by IR). IR (acetonitrile): $\nu(\text{CO})$ 2069(s), 1989(vs) cm^{-1} . $^1\text{H NMR}$ (CDCl_3): δ 2.17(s), δ 5.44(s) ppm.

3.9. Reaction of $\text{Ru}(\text{CO})_3(\text{NCCH}=\text{CH}_2)(\text{NCMe})$ (**10**) with excess of acrylonitrile

An excess of acrylonitrile was added to an acetonitrile solution of $\text{Ru}(\text{CO})_3(\text{NCCH}=\text{CH}_2)(\text{NCMe})$ (100 mg) and the mixture stirred. The bis-acrylonitrile complex $\text{Ru}(\text{CO})_3(\text{NCCH}=\text{CH}_2)_2$ (**11**) was formed (yield,

quantitative by IR). IR (acetonitrile): $\nu(\text{CO})$ 1947(vs) cm^{-1} . $^1\text{H NMR}$ (CDCl_3): δ 2.24(s), 2.85(s) ppm.

Acknowledgements

We acknowledge the support of the EPSRC for A.J.E. and N.E.L. We are grateful to Johnson Matthey plc for the loan of ruthenium trichloride.

References

- [1] B.F.G. Johnson, J. Lewis and M.V. Twigg, *J. Organomet. Chem.*, **67** (1974) C75.
- [2] M.I. Bruce and F.G.A. Stone, *J. Chem. Soc.* (1967) 1238.
- [3] M.R. Churchill, C.H. Lake, F.J. Saafarowic, D.S. Parfitt, L.R. Nevinger and J.B. Keister, *Organometallics*, **12** (1993) 671.
- [4] S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda and N. Chatani, *Nature*, **366** (1994) 529.
- [5] S. Cenini, S. Giordano, M. Pizzotti and F. Porta, *J. Organomet. Chem.*, **150** (1978) 261.
- [6] P.F. Ford, *J. Organomet. Chem.*, **383** (1990) 339.
- [7] G. Bor, *Inorg. Chim. Acta*, **1** (1967) 81.
- [8] M.I. Bruce, *Coord. Chem. Rev.*, **76** (1987) 1.
- [9] B.F.G. Johnson, J. Lewis and M.V. Twigg, *J. Chem. Soc., Chem. Commun.*, (1975) 1876.
- [10] E.E. Siefert and R. Angelici, *J. Organomet. Chem.*, **8** (1967) 374.