Journal of Organometallic Chemistry, 408 (1991) 233–239
Elsevier Sequoia S.A., Lausanne

JOM 21698

The formation of alkenedithiocarboxylate and alkenecarboxylate ligands by insertion of CS_2 and CO_2 into ruthenium(II)–alkenyl bonds

Hassane Loumrhari, Josep Ros *, Ramon Yáñez
Departament de Química, Universitat Autònoma de Barcelona, 08193-Bellaterra, Barcelona (Spain)

and M. Rosario Torres
Instituto de Química-Física "Rocasolano" C.S.I.C., Serrano 119, 28006-Madrid (Spain)

(Received September 20th, 1990)

Abstract

The unsaturated alkenyl complexes $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ react with CS_2 and CO_2 to give $Ru(CO)Cl(S_2CRC{=}CHR')(PPh_3)_2$ and $Ru(CO)Cl(O_2CRC{=}CHR')(PPh_3)_2$ complexes, respectively. The products are hexacoordinated-ruthenium(II) complexes containing alkenedithiocarboxylate or alkenecarboxylate ligands η^2-coordinated to metal. In these reactions CS_2 and CO_2 insert into ruthenium–alkenyl bonds to form new chelated ligands. The structures of products and the nature of the alkenedithiocarboxylate and alkenecarboxylate ligands have been established from spectroscopic data (IR, ^1H and ^{31}P NMR).

Introduction

The coordinatively unsaturated $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ complexes react readily with coordinating molecules such as CO [1] or CN^tBu [2] to give octahedral complexes containing acyl ligands. The η^2-acyl complex $Ru(CO)Cl(\eta^2\text{-}O{=}CCMe{=}CMeH)(PPh_3)_2$ obtained from the reaction of the $Ru(CO)Cl(CMe{=}CMeH)(PPh_3)_2$ complex with CO is slowly transformed in methanol to the complex $Ru(CO)Cl(\eta^2\text{-}O_2CCMe{=}CMeH)(PPh_3)_2$, the structure of which was confirmed by an X-ray diffraction study [1]. Reaction of CS_2 with some $Ru(CO)Cl(HC{=}CRH)(PPh_3)_2$ (R = Ph or ^tBu) complexes gave $Ru(CO)Cl(\eta^2\text{-}S_2CCH{=}CRH)(PPh_3)_2$ derivatives [3]. Other ruthenium(II) alkenyl complexes containing carboxylate [4,5] and dithiocarboxylate [6] ligands were recently prepared by our group by substitution of the chloride ligand by carboxylate or dithiocarboxylate anions. Because of the interest in insertions of CS_2 and CO_2 into metal–carbon bonds [7–9] a systematic study of the reactivity of these molecules with the coordinatively unsaturated complexes $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ was undertaken.

0022-328X/91/$03.50

Results and discussion

Reaction with CS_2

In an earlier communication we described the reaction of $Ru(CO)Cl(HC{=}CHR')(PPh_3)_2$ ($R' = {}^tBu$, Ph) complexes with CS_2 in refluxing CH_2Cl_2 [3] to give complexes of the type $Ru(CO)Cl(\eta^2\text{-}S_2CCH{=}CHR')(PPh_3)_2$. We have found that the $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ complexes react with a five-fold excess of CS_2 in a CH_2Cl_2 to give $Ru(CO)Cl(\eta^2\text{-}S_2CCR{=}CHR')(PPh_3)_2$ ($R = R' {=} H$, Me, Ph and CO_2Me; R = H and R' = Ph, ${}^tBu$, $SiMe_3$, CO_2Me, CO_2Et) complexes in virtually quantitative yield. The red products are moderately air-stable, soluble in

Table 1

IR and ^1H NMR data for complexes $Ru(CO)Cl(S_2CRC{=}CHR')(PPh_3)_2$

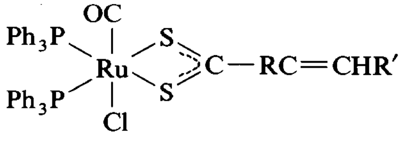
RC=CHR'	IR (ν (cm^{-1}))			^1H NMR (δ (ppm))	
	CO	C=C	SCS		
$HC{=}CH_2$	1945	–	1217	5.99	d, J 18 Hz, 1H
(**1**)			945	6.78	d, J 12 Hz, 1H
				7.2–7.7	m, 6P+1H
$HC{=}CHCMe_3$	1954	–	1214	1.02s,	3Me
(**2**)			907	6.21	d, J 16 Hz, 1H
				6.71	d, J 16 Hz, 1H
				7.3–7.8	m, 6Ph
$HC{=}CHSiMe_3$	1949	–	1218	0.9	s, 3Me
(**3**)			922	6.02	d, J 12 Hz, 1H
				6.80	d, J 12 Hz, 1H
				7.3–7.7	m, 6Ph
HC=CHPh	1940	1571	1222	6.88	d, J 16 Hz, 1H
(**4**)			949	6.75–7.7	m, 7Ph+1H
MeC=CHMe	1949	1618	1335	1.44	d, J 8 Hz, 1Me
(**5**)			990	1.55	s, 1Me
				5.90	q, J 8 Hz, 1H
				7.2–7.7	m, 6Ph
PhC=CHPh	1959	–	1305	5.37	s, 1H
(**6**)			923	6.4–7.8	m, 8Ph
$HC{=}CCO_2Me$	1932	1544	–	3.14	s, 1Me
(**7**)	1690		–	5.68	d, J 8 Hz, 1H
				7.0–7.8	m, 6Ph
				9.42	d, J 8 Hz, 1H
$HC{=}CCO_2Et$	1929	1564	–	0.88	t, J 5.6 Hz, 1Me
(**8**)	1655		923	3.51	q, J 5.6 Hz, $1CH_2$
				5.59	d, J 8 Hz, 1H
				7.1–7.9	m, 6Ph
				9.36	d, J 8 Hz, 1H
$MeO_2CC{=}CHCO_2Me$	1940	1558	–	3.20	s, 1Me
(**9**)	1703		923	3.30	s, 1Me
				4.91	s, 1H
				7.3–7.6	m, 6Ph

CH_2Cl_2 but insoluble in diethyl ether, alcohols, and petroleum ether. The analytical and spectroscopic data are in accord with the addition of one molecule of CS_2 to the unsaturated alkenyl compound (Table 1).

The IR spectra of the complexes confirm the presence of the η^2-coordinated alkenedithiocarboxylate group. The $\nu(S_2C)_{asym}$ and $\nu(S_2C)_{sym}$ bands are observed at ca. 1200 and 915 cm^{-1}, respectively, in most of complexes [10]. The ν(C=C) band is often obscured by other intense bands but is located at ca. 1544–1618 cm^{-1}. The intense $\nu(C\equiv O)$ absorption is observed at ca. 1930–1959 cm^{-1} and is shifted towards higher energies relative to the corresponding band in the unsaturated alkenyl complexes $Ru(CO)Cl(CR{=}CHR')(PPh_3)_2$.

The ^1H NMR spectra of $Ru(CO)Cl(S_2CCR{=}CHR')(PPh_3)_2$ complexes show the characteristic signals of the coordinated ligands. When R = H the signals of hydrogens in the $-CH_\alpha{=}CH_\beta R'$ group are observed as doublets with $J(H-H) = 12-16$ Hz, indicating a *trans*-disposition of the hydrogens. These signals are shifted from their positions in the unsaturated $Ru(CO)Cl(CR{=}CHR')(PPh_3)_2$ complexes [11,12]. The H_β hydrogens appear at ca. 6.7 ppm when R′ = H, ^tBu, $SiMe_3$ and Ph, and at ca. 5.6 ppm when R′ is an ester group. The H_α signals are often hidden by the phenyl multiplets but are located at ca. 6.7–9.4 ppm. The low field values for H_α are characteristic of $R' = CO_2Me$ and CO_2Et derivatives. The signal of the alkenyl proton in the disubstituted derivatives is observed at ca. 5–6 ppm.

The crystal structure of the $Ru(CO)Cl(\eta^2\text{-}S_2CCH{=}CHPh)(PPh_3)_2$ complex revealed a *cis*-disposition of the PPh_3 ligands [3]. In related dithioformate complexes $MX(S_2CH)(CO)(PR_3)_2$ (M = Ru, Os; X = Cl, Br; R = Ph, Ph_2Me, $PhMe_2$), the *cis*-isomer was formed at room temperature but upon heating was converted into the *trans*-derivative [13]. In the case of other ruthenium(II) phosphoniodithiocarboxylate complexes $[RuH(CO)(S_2CPR_3)PCy_3)_2][BPh_4]$ (R = Et, Cy) the *cis*- and *trans*-isomers were formed at moderate temperatures [14]. On the other hand, the *cis* → *trans* isomerization did not occur in the case of the dithioformate complexes $IrCl_2(S_2CH)(PPh_3)_2$ [13]. The spectroscopic data for $Ru(CO)Cl(\eta^2\text{-}S_2CCR{=}CHR')(PPh_3)_2$ complexes synthesized at room temperature are identical to those obtained by prolonged reflux in CH_2Cl_2 [3], suggesting a similar stereochemistry. In order to confirm the position of the phoshines the ^1H-decoupled ^{31}P NMR spectra of some complexes were recorded, and showed a single resonance at ca. 31 ppm for all of them. These results are in accord with equivalence of the two phosphines in a *cis*-disposition. The proposed structure for the $Ru(CO)Cl(S_2CCR{=}CHR')(PPh_3)_2$ complexes is as follows.



Reaction with CO_2

The reaction of CO_2 with $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ complexes was examined under different conditions of temperature, pressure and solvent. A slow reaction was observed when the mixture was refluxed at atmospheric pressure in CH_2Cl_2, THF, or MeOH. After prolonged reflux intractable mixtures of organic compounds and complexes were formed. However, when solutions of the complexes

Table 2

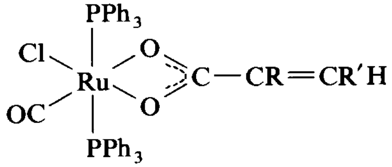
IR and ^{1}H NMR data for complexes Ru(CO)Cl(O$_2$CRC=CHR′)(PPh$_3$)$_2$

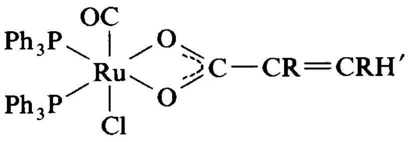
RC=CHR′	IR (ν (cm^{-1}))			^{1}H NMR (δ (ppm))		
	CO	C=C	OCO			
HC=CH$_2$	1943	1539	–	4.80	d,	*J* 12 Hz, 1H
(10)			1381	6.10	d,	*J* 18 Hz, 1H
				7.3–7.8	m,	6Ph+1H
HC=CHCMe$_3$	1940	1538	–	0.87	s,	3Me
(11)			1381	4.99	d,	*J* 18 Hz, 1H
				6.34	d,	*J* 18 Hz, 1H
				7.2–7.7	m,	6Ph
HC=CHSiMe$_3$	1940	1571	–	−0.66	s,	3Me
(12)			1381	5.45	d,	*J* 16 Hz, 1H
				7.2–7.9	m,	6Ph+1H
HC=CHPh	1941	1540	–	7.88	d,	*J* 18 Hz, 1H
(13)			1381	6.7–7.7	m,	7Ph+1H
MeC=CHMe	1943	1540	–	1.30	s,	1Me
(14)			1380	1.46	d,	*J* 8 Hz, 1Me
				4.26	q,	*J* 8 Hz, 1H
				7.2–7.7	m,	6Ph
PhC=CHPh	1944	1541	–	5.36	s,	1H
(15)			1380	6.2–7.8	m,	8Ph
HC=CHCO$_2$Me	1933	1546	–	3.45	s,	1Me
(16)	1697		1371	5.39	d,	*J* 12 Hz, 1H
				7–7.7	m,	6Ph+1H
HC=CHCO$_2$Et	1927	1557	–	0.89	t,	*J* 7.2 Hz, 1Me
(17)	1682		1371	3.83	q,	*J* 7.2 Hz, 1CH$_2$
				7.1–7.9	m,	6Ph
				9.60	d,	*J* 17 Hz, 1H
MeO$_2$CC=CHCO$_2$Me	1934	1559	–	3.39	s,	1Me
(18)	1712		1375	3.61	s,	1Me
				4.89	s,	1H
				7.3–7.7	m,	6Ph

Ru(CO)Cl(RC=CHR′)(PPh$_3$)$_2$ (R = R′ = H, Me, Ph and CO$_2$Me; R = H and R′ = Ph, ^{t}Bu, SiMe$_3$, CO$_2$Me, CO$_2$Et) in a CH$_2$Cl$_2$/MeOH mixture were treated in an autoclave with 1 atm of CO$_2$ for 1 h, a new family of green products was obtained. The complexes are moderately stable to air and are soluble in CH$_2$Cl$_2$ but insoluble in diethyl ether, alcohols and hydrocarbons. The elemental analyses and the spectroscopic data are in accord with formation of complexes of the type Ru(CO)Cl(η^2-O$_2$CCR=CHR′)(PPh$_3$)$_2$ which contain an alkenecarboxylate ligand coordinated through two oxygen atoms (Table 2). Other alkenecarboxylate ligands were obtained previously by coupling of ethylene with CO$_2$ in Mo and W complexes [15].

The solid IR spectra of Ru(CO)Cl(η^2-O$_2$CCR=CHR′)(PPh$_3$)$_2$ complexes display the typical bands of the alkenecarboxylate ligand. The ν(O$_2$C)$_{sym}$ band appears at ca. 1380 cm^{-1}, and the $\nu(O_2C)_{asym}$ and the ν(C=C) band appear at ca. 1540 cm^{-1}. Similar IR spectra were obtained for the recently reported 3,3-dimethylacrylate derivatives [5]. The $\nu(O_2C)$ and ν(C=C) bands are observed at lower energies than those for other carboxylate alkenyl Ru(II) complexes [4]. The ν(C≡O) absorptions appear at ca. 1927–1943 cm^{-1}, near the positions of the same bands for Ru(CO)Cl(η^2-S_2CCR=CHR′)$(PPh_3)_2$ complexes.

The ^{1}H NMR spectra of the complexes confirm the coupling of the alkenyl ligand with one molecule of CO_2. Thus, in the case of the terminal alkenyl derivatives the H_α and the H_β signals are observed at < 6.3 ppm and at ca. 4.9–5.5 ppm, respectively, as doublets with J(H–H) = 12–18 Hz, indicating a *trans*-disposition of the hydrogens. For the complexes containing disubstituted alkenyl ligands, the =C*H*R′ proton appears at ca. 4.3–5.4 ppm. The ^{1}H-decoupled ^{31}P NMR spectra of some Ru(CO)Cl(η^2-O_2CCR=CHR)$(PPh_3)_2$ complexes at room temperature display a single peak at 37.0–37.8 ppm, suggesting equivalence of the two PPh_3 ligands. The Ru(CO)Cl(η^2-O_2CCR=CHR′)$(PPh_3)_2$ complexes decompose slowly in solution showing, after some hours, ^{31}P NMR spectra with signals of the hydride complex Ru(CO)ClH$(PPh_3)_3$ and of other, unknown products. These spectroscopic data are consistent with the two possible structures for the complexes depicted below:





Experimental

The C and H elemental analyses were performed with a Perkin–Elmer 240B analyzer. The ^{1}H NMR spectra were recorded on a Bruker AM 400 spectrometer in $CDCl_3$ solution. The ^{1}H-decoupled ^{31}P NMR spectra were recorded on the same instrument in $CDCl_3$ solutions with aqueous 85% H_3PO_4 as external reference. The IR spectra were recorded on a Perkin–Elmer 1710-FT apparatus with KBr pellets.

The syntheses of the complexes were carried out under nitrogen by Schlenk techniques. The Ru(CO)Cl(RC=CHR′)$(PPh_3)_2$ complexes were prepared by previously described methods [11,12,16].

Preparation of Ru(CO)Cl(η^2-S_2CRC=CHR′)$(PPh_3)_2$ complexes

Carbon disulphide (5 ml) was added with stirring to 15 ml of a CH_2Cl_2 solution of 0.2 g of Ru(CO)Cl(RC=CHR′)$(PPh_3)_2$. The mixture, which turned red, was stirred for 4 h at room temperature, and then evaporated to dryness *in vacuo*. The residue was dissolved in 10 ml of CH_2Cl_2 and the product quantitatively precipitated by slow addition of petroleum ether. The red complexes can be recrystallized from CH_2Cl_2/MeOH mixtures.

Ru(CO)Cl(S_2CHC=CH_2)$(PPh_3)_2$ (**1**). Found: C, 60.63; H, 4.21. $C_{40}H_{33}$-$ClOP_2S_2Ru$ calc.: C, 60.44; H, 4.24%.

Ru(CO)Cl(S_2CHC=CH^{t}Bu)$(PPh_3)_2$ (**2**). Found: C, 62.28; H, 4.68. $C_{44}H_{41}$-$ClOP_2S_2Ru$ calc.: C, 62.87; H, 4.24%.

$Ru(CO)Cl(S_2CHC=CHSiMe_3)(PPh_3)_2$ (3). Found: C, 59.74; H, 4.79. $C_{43}H_{41}ClOP_2S_2SiRu$ calc.: C, 60.28; H, 4.58%.

$Ru(CO)Cl(S_2CHC=CHPh)(PPh_3)_2$ (4). Found: C, 63.62; H, 4.30. $C_{46}H_{37}ClOP_2S_2Ru$ calc.: C, 63.41; H, 4.38%. $\{^1H\}$-^{31}P NMR: δ 31.63 (s) ppm.

$Ru(CO)Cl(S_2CMeC=CHMe)(PPh_3)_2$ (5). Found: C, 64.41; H, 4.56. $C_{44}H_{37}ClOP_2S_2Ru$ calc.: C, 64.47; H, 4.42%.

$Ru(CO)Cl(S_2CPhC=CHPh)(PPh_3)_2$ (6). Found: C, 66.12; H, 4.38. $C_{52}H_{41}ClOP_2S_2Ru$ calc.: C, 66.14; H, 4.29%. $\{^1H\}$-^{31}P NMR: δ 30.54 (s) ppm.

$Ru(CO)Cl(S_2CHC=CHCO_2Me)(PPh_3)_2$ (7). Found: C, 59.32; H, 4.16. $C_{42}H_{35}ClO_3P_2S_2Ru$ calc.: C, 58.36; H, 4.00%.

$Ru(CO)Cl(S_2CHC=CHCO_2Et)(PPh_3)_2$ (8). Found: C, 59.75; H, 4.32. $C_{43}H_{37}ClO_3P_2S_2Ru$ calc.: C, 59.50; H, 4.37%. $\{^1H\}$-^{31}P NMR: δ 31.13 (s) ppm.

$Ru(CO)Cl(S_2CMeO_2CC=CHCO_2Me)(PPh_3)_2$ (9). Found: C, 58.18; H, 4.11. $C_{44}H_{37}ClO_5P_2S_2Ru$ calc.: C, 58.10; H, 4.06%.

Preparation of $Ru(CO)Cl(\eta^2\text{-}O_2CRC=CHR')(PPh_3)_2$ complexes

A solution of 0.2 g of $Ru(CO)Cl(RC=CHR')(PPh_3)_2$ in 20 ml of a 1 : 1 mixture of CH_2Cl_2 and MeOH was placed in an autoclave which was then charged with 1 atm of CO_2. After 1 h stirring at room temperature the green solution was transferred to a suitable vessel and evaporated to dryness *in vacuo*. The residue was dissolved in a minimum of CH_2Cl_2 and the crude product precipitated by addition of petroleum ether. The products, which were green, were purified by three washings with petroleum ether, then dried *in vacuo*. The yield was > 60%.

$Ru(CO)Cl(O_2CHC=CH_2)(PPh_3)_2$ (10). Found: C, 63.20; H, 4.38. $C_{40}H_{33}ClO_3P_2$ calc.: C, 64.80; H, 4.90%.

$Ru(CO)Cl(O_2CHC=CH^tBu)(PPh_3)_2$ (11). Found: C, 64.74; H, 5.07. $C_{44}H_{41}ClO_3P_2Ru$ calc.: C, 64.44; H, 5.35%, $\{^1H\}$ ^{31}P NMR: δ 37.23 (s) ppm.

$Ru(CO)Cl(O_2CHC=CHSiMe_3)(PPh_3)_2$ (12). Found: C, 62.04; H, 4.97. $C_{43}H_{41}ClO_3P_2SiRu$ calc.: C, 61.47; H, 5.02%. $\{^1H\}$-^{31}P NMR: δ 37.19 (s) ppm.

$Ru(CO)Cl(O_2CHC=CHPh)(PPh_3)_2$ (13). Found: C, 66.06; H, 4.47. $C_{46}H_{37}ClO_3P_2Ru$ calc.: C, 66.40; H, 4.90%. $\{^1H\}$-^{31}P NMR: δ 37.01 (s) ppm.

$Ru(CO)Cl(O_2CMeC=CHMe)(PPh_3)_2$ (14). Found: C, 63.99; H, 4.74. $C_{42}H_{37}ClO_32P_2Ru$ calc.: C, 64.17; H, 5.17%. $\{^1H\}$-^{31}P NMR: δ 37.39 (s) ppm.

$Ru(CO)Cl(O_2CPhC=CHPh)(PPh_3)_2$ (15). Found: C, 67.13; H, 4.54. $C_{52}H_{42}ClO_3P_2Ru$ calc.: C, 68.15; H, 5.25%. $\{^1H\}$-^{31}P NMR: δ 37.45 (br) ppm.

$Ru(CO)Cl(O_2CHC=CHCO_2Me)(PPh_3)_2$ (16). Found: C, 61.65; H, 4.32. $C_{42}H_{35}ClO_5P_2Ru$ calc.: C, 61.82; H, 5.09%.

$Ru(CO)Cl(O_2CHC=CHCO_2Et)(PPh_3)_2$ (17). Found: C, 62.05; H, 4.49. $C_{43}H_{37}ClO_5P_2Ru$ calc.: C, 61.89; H, 4.69%. $\{^1H\}$-^{31}P NMR: δ 37.48 (s) ppm.

$Ru(CO)Cl(O_2CMeO_2CC=CHCO_2Me)(PPh_3)_2$ (18). Found: C, 60.03; H, 4.26. $C_{44}H_{37}ClO_7P_2Ru$ calc.: C, 60.73; H, 5.02%.

Acknowledgements

Financial support of the DGICYT of Spain (Project No. PB87-0201-C03-03) is gratefully acknowledged. H.L. thanks the Ministère de l'Education Nationale du Maroc for a fellowship.

References

1 M.R. Torres, A. Perales, H. Loumrhari and J. Ros, J. Organomet. Chem., 384 (1990) C61.
2 J. Montoya, A. Santos, A.M. Echavarren and J. Ros, J. Organomet. Chem., 390 (1980) C57.
3 M.R. Torres, A. Perales and J. Ros, Organometallics, 7 (1988) 1223.
4 M.R. Torres, A. Perales, H. Loumrhari and J. Ros, J. Organomet. Chem., 385 (1990) 379.
5 H. Loumrhari, J. Ros, M.R. Torres and A. Perales, Polyhedron, 9 (1990) 907.
6 H. Loumrhari, J. Ros and M.R. Torres, Polyhedron, accepted for publication.
7 A. Behr, in Carbon Dioxide Activation by Metal Complexes, VCH Publishers, Weinheim, 1988, p. 46.
8 G. Wilkinson, F.G. Stone and E. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 8, Ch. 50.4, p. 225.
9 A. Behr, Angew. Chem., Int. Ed. Engl., 27 (1988) 661.
10 P.V. Yaneff, Coord. Chem. Rev., 23 (1977) 183.
11 M.R. Torres, A. Vegas, A. Santos and J. Ros, J. Organomet. Chem., 326 (1987) 413.
12 M.R. Torres, A. Vegas, A. Santos, J. Ros and X. Solans, Organometallics, 6 (1987) 1091.
13 S.D. Robinson and A. Sahajpal, Inorg. Chem., 16 (1977) 2718.
14 T.R. Gaffney and J.A. Ibers, Inorg. Chem., 21 (1982) 2062.
15 R. Alvarez, E. Carmona, A. Galindo, E. Gutierrez, J.M. Marín, A. Monge, M.L. Poveda, C. Ruiz and J.M. Savariault, Organometallics, 8 (1989) 2430.
16 M.R. Torres, A. Vegas, A. Santos and J. Ros, J. Organomet. Chem., 309 (1986) 169.