ELSEVIER

Journal of Organometallic Chemistry 545–546 (1997) 79–87

Journal of Organometallic Chemistry

Metal complexes with atropisomeric sulfur ligands in asymmetric hydroformylation X-ray structure of $[Rh_2(\mu\text{-biphes})(cod)_2]$ (H_2biphes = 4,4′-biphenanthrene-3,3′-dithiol)

Nuria Ruiz [a], Abdellatif Aaliti [a,b], Jorge Forniés-Cámer [a], Aurora Ruiz [a], Carmen Claver [a,*], Christine J. Cardin [c], Davide Fabbri [d], Serafino Gladiali [e,*]

[a] *Departament de Química, Universitat Rovira i Virgili, Pl. Imperial Tarraco 1, 43005 Tarragona, Spain*
[b] *Département de Chimie, Université Abdelmalek Essaadi, Tétouan, Morocco*
[c] *Department of Chemistry, The University of Reading, Whiteknights, PO Box 224, Reading RG6 6AD, UK*
[d] *Istituto CNR per l'Applicazione delle Technique Chimiche Avanzate ai Problemi Agrobiologici, Via Vienna 2, 07100 Sassari, Italy*
[e] *Dipartimento di Chimica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy*

Received 18 December 1996

Abstract

The addition of the atropisomeric racemic sulfur compound 4,4′-biphenanthrene-3,3′-dithiol (H_2biphes) to a dichloromethane solution of $[\{M(\mu\text{-OMe})(cod)\}_2]$ (M = Rh, Ir, cod = cycloocta-1,5-diene) afforded the dithiolate-bridged complexes $[\{Rh_2(\mu\text{-biphes})(cod)_2\}_n]$ ($n = 2$ **5** or $n = 1$ **6**) and $[\{Ir_2(\mu\text{-biphes})(cod)_2\}_n]\cdot{}_nCH_2Cl_2$ **7**. When 1,1′-binaphthalene-2,2′-dithiol (H_2binas) reacted with $[\{Ir(\mu\text{-OMe})(cod)\}_2]$, complex $[Ir_2(\mu\text{-binas})(cod)_2]$ **8** was obtained. Complexes **5** and **6** reacted with carbon monoxide to give the dinuclear tetracarbonyl complex $[Rh_2(\mu\text{-biphes})(CO)_4]$ **9**. The reaction of **9** with PR_3 provided the mixed-ligand complexes $[\{Rh_2(\mu\text{-biphes})(CO)_2(PR_3)_2\}_2]\cdot xCH_2Cl_2$ (R = Ph, $x = 2$ **10**, C_6H_{11}, $x = 1$ **11**) and $[\{Rh_2(\mu\text{-biphes})(CO)_3(PR_3)\}_2]\cdot CH_2Cl_2$ **12** (R = $OC_6H_4Bu^t$-*o*). The crystal structure of **6** was determined by X-ray diffraction. Reaction of the dithioether ligand Me_2biphes with $[Rh(cod)_2]ClO_4$ in CH_2Cl_2 solution afforded the cationic complex $[Rh(cod)(Me_2biphes)]ClO_4\cdot CH_2Cl_2$ **13**. Asymmetric hydroformylation of styrene was performed using the complexes described. The extent of aldehyde conversion ranges from 53 to 100%, with selectivities towards branched aldehydes in the range 51 to 96%. The enantioselectivities were quite low and did not exceed 20%. © 1997 Elsevier Science S.A.

Keywords: Rhodium; Iridium; Atropisomeric sulfur ligands; Asymmetric hydroformylation

1. Introduction

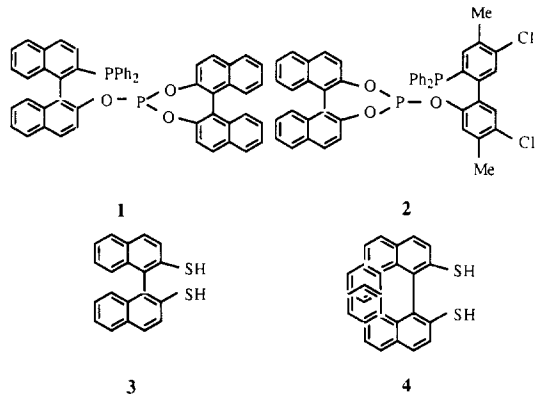
The regio and enantioselective hydroformylation of olefins is a reaction of great chemical and pharmaceutical interest because it provides a straightforward method for the synthesis of chiral aldehydes [1]. These are valuable intermediates in the preparation of a wide variety of products of biological interest [2].

Rhodium catalysts display high activity in hydroformylation and, in the case of aryl-substituted ethylenes, they produce the branched aldehyde in high yield with excellent chemo- and regio-selectivity even at low temperature and moderate pressure [1]. The enantioselectivity of this reaction, however, varies over a wide range, and high enantiomeric excesses (*e.e.*s) have been attained only in the last 3 years, following the introduction of chiral bidentate ligands with phosphorus donors of new design. Notably, most of these ligands have a stereogenic axis as a chiral motif.

For instance, Takaya and coworkers have demonstrated that complexes with the atropisomeric mixed phosphine phosphite ligand (*S,R*)- and (*R,S*)-binaphos **1** or biphemphos **2** (Scheme 1) are excellent catalysts for the enantioselective hydroformylation of a variety of terminal and internal olefins [3]. On the other hand, different catalytic precursors derived from chiral

* Corresponding author.

0022-328X/97/$17.00 © 1997 Elsevier Science S.A. All rights reserved.
PII S0022-328X(97)00151-4



Scheme 1.

diphosphites and diphosphinites have provided *e.e.*s between 50 and 90% in the hydroformylation of styrene while retaining the excellent chemo- and regio-selectivity typical of rhodium catalysts [4]. These results are illustrative of the ability of these novel chiral phosphorus chelators to induce asymmetry in rhodium-catalyzed hydroformylation.

The high catalytic activity displayed in hydroformylation by dinuclear thiolato-bridged rhodium complexes has been documented for several years [5,6].

The first demonstration that chiral rhodium catalysts containing sulfur ligands can induce asymmetry in hydroformylation has been established only 3 years ago. Our groups [7] showed that styrene can be hydroformylated by Rh(I) complexes containing either anionic or neutral ligands derived from the atropisomeric binaphthalene-core dithiol H_2binas **3** (Scheme 1). Although the stereoselectivity was low and did not exceed 15% *e.e.*, this was considered to be a significant result because the use of chiral ligands containing only sulfur as a donor provided new opportunities in asymmetric hydroformylation and, more generally, in asymmetric catalysis promoted by organotransition metal complexes.

High catalytic activity and regioselectivity were also recorded both when using cationic mononuclear and neutral dinuclear Rh(I) complexes as catalytic precursors [7]. While some of these derivatives have been isolated and characterized by multinuclear NMR in an early stage of this investigation, more recently a mixed carbonyl phosphite tetranuclear rhodium dithiolato complex $[\{Rh_2(\mu\text{-binas})(CO)_3(P(OC_6H_4Bu^t\text{-}o)_3)\}_2]$ has been isolated and its crystal structure determined by X-ray diffraction [8].

Pursuing our efforts in this field, we have extended the investigation of binas-based catalysts in asymmetric hydroformylation. More recently, we have introduced different sulfur donor atropisomeric ligands based on the axially chiral biphenanthrene backbone for use in this process. Compounds of this structure have recently been prepared in enantiopure form in order to check if an increase of the conformational stability and of the stiffness of the atropisomeric diaryl framework could result in an improved asymmetric induction with respect to the corresponding binaphthalene counterparts [9].

Here we report on new rhodium(I) and iridium(I) derivatives containing neutral or anionic sulfur ligands derived from 4,4′-biphenanthrene-3,3′-dithiol **4** (H_2biphes) (Scheme 1) and on the catalytic activity of some of these complexes and the analogous ones with binas in the enantioselective hydroformylation of styrene.

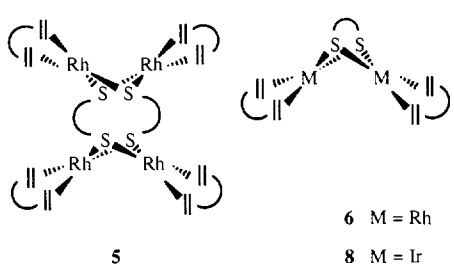
2. Results and discussion

2.1. Preparation of the dithiolate complexes

Complexes $[\{Rh_2(\mu\text{-biphes})(cod)_2\}_n]$ $n = 2$ **5** and $n = 1$ **6** and $[\{Ir_2(\mu\text{-biphes})(cod)_2\}_n] \cdot nCH_2Cl_2$ **7** (cod = 1,5-cyclooctadiene) were obtained by adding racemic H_2biphes to a dichloromethane solution of $[\{M(\mu\text{-OMe})(cod)\}_2]$ (M = Rh, Ir). When racemic H_2binas was added to a dichloromethane solution of $[\{Ir(\mu\text{-OMe})(cod)\}_2]$, complex $[Ir(\mu\text{-binas})(cod)_2]$ **8** was formed. The reactions are analogous to that reported for rhodium complexes with the binas ligand [8]. In the case of rhodium complexes, the addition of methanol caused the precipitation of an orange solid **5** whose microanalytical data matches the $[\{Rh_2(\mu\text{-biphes})(cod)_2\}_n]$ stoichiometry. The concentration and cooling of the remaining solution yielded a red complex **6** which corresponded to the same stoichiometry. In the case of iridium complexes, dark red solids **7** and **8** were isolated by addition of methanol.

The molecular weights of the complexes **5**, **6** and **8**, determined osmometrically in CH_2Cl_2 at 25 °C indicate that **5** is tetranuclear and **6** and **8** are dinuclear (Scheme 2). The molecular ion for **6** ($m/z = 838$) is the heaviest ion in the FAB mass spectra of both **5** and **6**, which suggests that **5** undergoes fragmentation. In the case of **7**, the molecular weight was not able to be determined and its FAB mass spectrum shows the heaviest ion at $m/z = 1017$ which does not allow one to conclude the nuclearity.

The ^{1}H NMR spectra for **5** and **6** show the olefinic proton signals of the coordinated cyclooctadiene ligand



Scheme 2.

as two multiplets at δ 4.2 and 4.5 ppm and for **7** and **8** at δ 3.6 and 4.2 ppm. Owing to the bent structure and to the nature of the dithiolate ligand, four non-equivalent sites should be expected. However, not all non-equivalences were resolved. The methylenic protons show two multiplets at 1.8 and 2.2 ppm for **5** and **6** and at 1.8 and 2.0 ppm for **7** and **8**. The different signals corresponding to the aromatic protons of the coordinated dithiolate ligand can be seen at 6.0–8.2 ppm. ^{1}H NMR of the rhodium complexes **5** and **6** do not show differences, as would be expected according to the osmometric measurements.

The structure of the complex **6** was established by an X-ray diffraction study. The molecular structure of **6** is presented in Fig. 1. Selected bonds and angles are listed in Table 1. Data collection parameters are summarized in Table 2. Suitable crystals were obtained for the complex synthesized with a raceme mixture of the biphes ligand, just as is corroborated with the structure analysis. The ligand bridges the two metals atoms which present an almost square-planar environment. The torsion angle between the two metals and the sulfur atoms is 116.3°. The intramolecular Rh(1)–Rh(2) distance 2.948 Å suggests a weak metal–metal interaction [10,11]. This distance is slightly longer than other dirhodium complexes which have bridging dithiolate ligands, $[Rh_2(\mu\text{-}(S(CH_2)_2S)(cod)_2]$ (Rh–Rh = 2.876 Å), $[Rh_2(\mu\text{-}(S(CH_2)_3S)(cod)_2]$ (Rh–Rh = 2.896 Å) [12]. Otherwise this distance is similar to one in the asymmetric unit of the tetranuclear Rh(I) complex with binas ligand $[\{Rh_2(\mu\text{-binas})(CO)_3(P(OC_6H_4Bu^t\text{-}o)_3)\}_2]$ [8]. The shortest intermolecular distance between two different molecules is 6.048 Å. This distance indicates no interaction between metal atoms of different molecules. The Rh–S distance (average 2.402 Å) and Rh–C distance (average 2.169 Å) are similar to other complexes with dithiolate-bridged ligands [12,13].

This is the first example of a dirhodium complex with an atropisomeric dithiol structurally characterized.

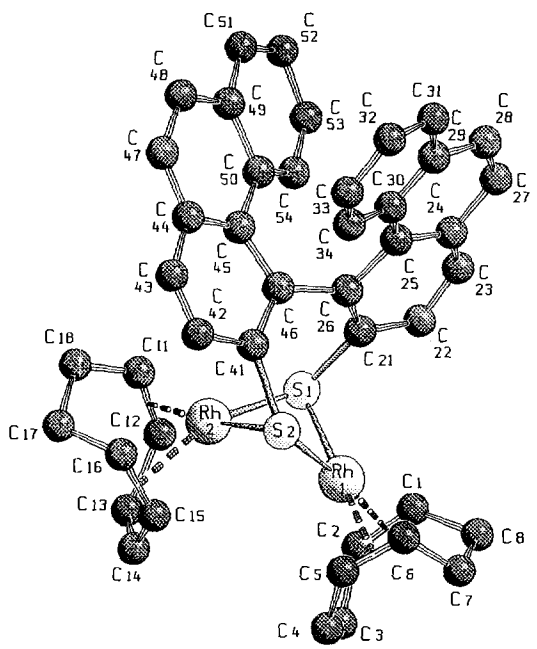


Fig. 1. Molecular structure of $[Rh_2(\mu\text{-biphes})(cod)_2]$ **6**.

Table 1
Selected bond lengths (Å) and angles (deg) for complex **6**

Rh(1)–Rh(2)	2.948(1)		
Rh(1)–S(1)	2.487(2)	Rh(2)–S(1)	2.380(2)
Rh(1)–S(2)	2.367(2)	Rh(2)–S(2)	2.374(2)
Rh(1)–C(1)	2.16(1)	Rh(2)–C(11)	2.19(1)
Rh(1)–C(2)	2.17(1)	Rh(2)–C(12)	2.19(1)
Rh(1)–C(5)	2.15(1)	Rh(2)–C(15)	2.15(1)
Rh(1)–C(6)	2.19(1)	Rh(2)–C(16)	2.16(1)
S(1)–C(21)	1.815(8)	S(2)–C(41)	1.807(8)
Rh(1)–M1	2.056	Rh(1)–M2	2.051
Rh(2)–M3	2.080	Rh(2)–M4	2.045
Rh(1)–S(2)–Rh(2)	76.89(6)	Rh(2)–S(1)–Rh(1)	74.52(6)
S(2)–Rh(1)–S(1)	86.70(7)	S(2)–Rh(2)–S(1)	88.94(7)
M1–Rh(1)–M2	87.06	M1–Rh(1)–S(1)	97.39
M1–Rh(1)–S(2)	159.55	M2–Rh(1)–S(2)	90.84
M2–Rh(1)–S(1)	173.59	M3–Rh(2)–M4	87.28
M3–Rh(2)–S(1)	89.69	M3–Rh(2)–S(2)	178.62
M4–Rh(2)–S(2)	94.09	M4–Rh(2)–S(1)	171.29

M1, M2, M3 and M4 are the midpoints of C(1)–C(2), C(5)–C(6), C(11)–C(12), C(15)–C(16) respectively.

Table 2
Crystal data for compound **6**

Empirical formula	$C_{44}H_{40}Rh_2S_2$
Formula weight	838.70
Temperature (K)	293
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 10.95(6)$ Å
	$b = 26.87(6)$ Å, $\beta = 103.12(6)°$,
	$c = 12.68(6)$ Å
Volume (Å^3)	3633.3
Z	4
Density (calculated) (g cm^{-3})	1.533
Absorption coefficient (mm^{-1})	1.054
$F(000)$	1704
Crystal size (mm^3)	0.2×0.2×0.1
θ range for data collection (deg)	2.22 to 24.99
Index ranges	$0 \le h \le 12$, $0 \le k \le 31$,
	$-14 \le l \le 14$
Reflections collected	21678
Independent reflections	5842 [R(int) = 0.0587]
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	5713/0/515
Goodness-of-fit on F^2	1.222
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0652$, $wR2 = 0.1389$
R indices (all data)	$R_2 = 0.0867$, $wR2 = 0.1698$
Largest diff. peak and hole (e$^-$ Å^{-3})	0.819 and −0.920

Bubbling carbon monoxide through dichloromethane solutions of the diene completes **5** and **6** yields carbonyl complexes which are formed by displacing the diene. The elemental analyses match the stoichiometry $[\{Rh_2(\mu\text{-biphes})(CO)_4\}_n]$ **9**. The molecular weight (791) was determined osmometrically and suggested that a dinuclear compound had been formed. Monitoring the reaction by infrared spectroscopy shows the presence of three ν(CO) signals at 2076m, 2061s and 2014s cm^{-1} which are characteristic of dinuclear tetracarbonyl rhodium complexes [8,11,14–16].

On treatment with PR_3 (R = Ph, C_6H_{11}, $OC_6H_4Bu^t$-*o*), the dinuclear tetracarbonyl complex $[Rh_2(\mu\text{-biphes})(CO)_4]$ **9** affords the carbonyl–phosphorus complexes $[\{Rh_2(\mu\text{-biphes})(CO)_2(PR_3)_2\}_2]\cdot xCH_2Cl_2$ (R = Ph, $x = 2$ **10**, R = C_6H_{11}, $x = 1$ **11**) and $[\{Rh_2(\mu\text{-biphes})(CO)_3(PR_3)\}_2]\cdot CH_2Cl_2$ **12** (R = $OC_6H_4Bu^t$-*o*). The molecular weights, determined osmometrically in CH_2Cl_2 at 25 °C indicate the tetranuclearity of the complexes.

The IR spectra in CH_2Cl_2 and KBr of **10**, **11** and **12** show ν(CO) absorptions corresponding to terminal carbonyl complexes.

The ^{31}P NMR spectrum of **10** in $CDCl_3$ shows a doublet at δ (ppm) = 45.4 (^1J(Rh–P) = 174 Hz) indicating that the phosphorus ligands are in equivalent environments. The ^{31}P NMR in $CDCl_3$ of **11** shows one doublet of high intensity at δ (ppm) = 35.52 (^1J(Rh–P) = 124 Hz) and another doublet of lower intensity at δ (ppm) = 36.98 (^1J(Rh–P) = 118 Hz) which is indicative of different environments for the phosphorus ligand.

Elemental analysis of **12** indicates that only two of the CO ligands are substituted by a phosphorus ligand, as we reported previously in the structure of the complex $[\{Rh_2(\mu\text{-binas})(CO)_3(P(OC_6H_4Bu^t\text{-}o)_3)\}_2]$ where binas ligand was used [8]. The behavior of $P(OC_6H_4Bu^t\text{-}o)_3$ ligand is analogous for Rh–biphes complexes. The ^{31}P NMR spectrum of **12** in $CDCl_3$ shows a broad signal at δ (ppm) = 119 which is not possible to resolve, either by changing solvent or by decreasing the temperature to −120 °C.

2.2. Preparation of the dithioether complex

Reaction of Me_2biphes with $[Rh(cod)_2]ClO_4$ in CH_2Cl_2 solution and addition of diethyl ether afforded the cationic complex $[Rh(cod)(Me_2biphes)]ClO_4\cdot CH_2Cl_2$ **13** by displacement of one 1,5-cyclooctadiene ligand. Microanalytical data matches the stoichiometry presented.

The FAB mass spectrum shows the heaviest ion at $m/z = 657$ corresponding to the loss of ClO_4^- in the molecular ion. This is indicative of a mononuclear complex.

The IR spectrum in KBr shows two strong bands at 1100 and 620 cm^{-1} which are characteristic of the ClO_4^- anion in cationic rhodium complexes.

^1H NMR in $CDCl_3$ shows two multiplets at δ 4.2 and 3.8 ppm which correspond to the olefinic protons of the coordinated cyclooctadiene and two multiplets at δ 2.5 and 1.8 ppm which correspond to the endo and exo methylenic protons. Methyl groups of the Me_2biphes ligand appear as a singlet at δ 2.2 ppm. The different signals corresponding to the aromatic protons of the coordinated dithioether ligand can be observed in the region 8.1–5.9 ppm.

When other dithioether ligands, $(iPr)_2$binas and $(iPr)_2$biphes, were used no reaction was observed at room temperature.

2.3. Hydroformylation of styrene

Catalytic experiments were run in tetrahydrofurane at a substrate/metal ratio 400:1 under different operative conditions in order to check the influence of the most significant parameters. Preformed neutral dinuclear or cationic mononuclear complexes were normally employed as catalysts. Preliminary experiments were carried out using racemic ligands. Enantiopure ligands were used when the more favorable conditions were met.

2.3.1. Precursor systems based on neutral $[Rh_2(\mu\text{-dithiolato})(cod)_2]$ complexes

Dithiolate-bridged rhodium complexes $[Rh_2(\mu\text{-dithiolato})(cod)_2]$ in the absence of additional phosphorus

Table 3
Hydroformylation of styrene with neutral $[Rh_2(\mu\text{-dithiolato})(cod)_2]$ complexes

Entry	Dithiolato	*P* (atm)	*T* (°C)	*t* (h)	L	Conv. (%)[b]	iso (%)	*e.e.* (%)
1	binas	5	80	24	$4PPh_3$	80	85	—
2[a]	binas	30	80	24	—	77	56	11
3	binas	80	60	6	—	92	91	—
				21		97	91	—
4	binas	30	80	3	$4PPh_3$	100	92	—
5[a]	binas	30	60	4	$4PPh_3$	100	92	7
6	binas	80	40	7	$10PPh_3$	88	93	—
7	binas	30	40	20	$10PPh_3$	98	94	—
8	biphes	30	80	24	—	97	52	—
9	biphes	80	60	6	—	80	89	—
				24		100	89	—
10	biphes	30	80	48	$4PPh_3$	67	87	—
				72		100	86	—
11	biphes	30	60	42	$4PPh_3$	77	93	—
				56		100	91	—
12[a]	biphes	5	80	12	$4PPh_3$	88	76	4
13[a]	biphes	30	80	8	—	53	60	3

Reaction conditions. Solvent: THF; CO/H_2: 1/1; substrate/precursor: 400.
[a] Enantiomerically pure ligand used.
[b] Conversion into aldehydes.

ligand are active catalyst precursors at 30 bar and 80 °C in the hydroformylation of styrene (Table 3). Only conversion in aldehydes was obtained, and no hydrogenation or isomerization was observed. In all the experiments performed with enantiopure dithiols, the branched isomer showed a modest *e.e.*, as determined by GC on chiral column of the relevant alcohols obtained through $LiAlH_4$ reduction. The prevailing antipode always had the *S*-configuration when *R*-binas or *R*-biphes were used as chiral entertainers.

It is apparent from these results that, in the case of dithiolate-bridged complexes, the structure of the diaryl framework has a negligible influence, if any, on the selectivity of the catalyst. The only significant difference between these catalysts is observed in the runs performed at 30 atm in the presence of PPh_3 as a co-ligand where the binas derivative displays a remarkably higher catalytic activity with respect to the biphes counterpart (cf. entries 4–10 and 5–11). Notably, even in this case, chemo- and regio-selectivities were practically identical. This difference in the activity of both binas and biphes dithiolate systems can be considered as evidence of the modification of the system by the dithiolate ligand even at 30 bar of pressure and P/Rh = 2.

2.3.2. *Precursor systems based on cationic [Rh(dithioether)(cod)]$^+$ complexes*

Mononuclear cationic rhodium complexes with binas- and biphes-derived thioethers displayed a high catalytic activity (Table 4). When preformed complexes were not available, catalysts were prepared in situ by adding the appropriate amount of the ligand to a suitable Rh-complex, most usually $[Rh(cod)_2]X$ (X = ClO_4^-, BF_4^-). This in situ technique was routinely used with i-propyl thioethers of binas and biphes, which did not produce easily isolable derivatives upon reaction with $[Rh(cod)_2]X$ (X = ClO_4^-, BF_4^-). We confidently assume that the coordination to the metal precedes hydroformylation because comparable results were obtained with Me_2binas using the two different procedures under otherwise identical conditions and because quite different chemo- and regio-selectivities were observed when using plain $[Rh(cod)_2]X$ (X = ClO_4^-, BF_4^-) with no additional thioether ligand. These cationic systems are active in the absence of PPh_3 ligand, and one of the advantages is the possibility of varying the S/Rh ratio by addition of excess of dithioether ligands. Using Me_2binas, styrene could be hydroformylated at a reasonable rate even at room temperature, affording more than 80% conversion in 24 h with complete chemoselec-

Table 4
Hydroformylation of styrene with cationic [Rh(dithioether)(cod)]$^+$ complexes

Entry	Dithioether	*P* (atm)	*T* (°C)	*t* (h)	L	Conv. (%)[b]	iso (%)	*e.e.* (%)
14[a]	Me_2binas	30	80	24	—	98	51	6
15[a]	Me_2binas	80	80	24	—	91	70	8
16[a]	Me_2binas	30	80	24	3Me_2binas	90	53	13
17[a]	Me_2binas	80	80	24	3Me_2binas	100	84	15
18[a]	Me_2binas	80	60	24	3Me_2binas	100	91	3
19[a]	Me_2binas	80	40	3	3Me_2binas	60	93	3
				24		100	94	6
20[a]	Me_2binas	80	25	24	3Me_2binas	81	96	2
21	Me_2binas	30	80	24	2PPh_3	99	86	—
22	Me_2biphes	30	80	24	—	99	58	—
23	Me_2biphes	30	60	16	—	90	92	—
24[a]	Me_2biphes	30	80	10	3Me_2biphes	100	63	3
25[a]	Me_2biphes	80	80	8	3Me_2biphes	100	83	4
26[a]	Me_2biphes	80	40	4	3Me_2biphes	95	95	2
27	Me_2biphes	30	80	10	2PPh_3	97	89	—
28	Me_2biphes	30	40	20	2PPh_3	60	93	—
29	Me_2biphes	30	40	20	5PPh_3	62	92	—
30[a,c]	$(iPr)_2$binas	30	80	24	—	96	53	—
31[a,c]	$(iPr)_2$binas	80	80	12	3$(iPr)_2$binas	100	85	20
32[a,c]	$(iPr)_2$binas	80	40	30	3$(iPr)_2$binas	93	94	3
33[a,c]	$(iPr)_2$biphes	30	80	24	—	100	52	—
34[a,c]	$(iPr)_2$biphes	80	80	12	3$(iPr)_2$biphes	100	84	—
35[a,c]	$(iPr)_2$biphes	80	40	24	3$(iPr)_2$biphes	88	95	—
				40		100	95	—

Reaction conditions. Solvent: THF; CO/H_2: 1/1; substrate/precursor: 400.
[a] Enantiomerically pure ligand used.
[b] Conversion into aldehydes.
[c] In situ precursor $[Rh(cod)_2]^+$ + dithioether ligand.

tivity. The share of the branched aldehyde was favorably affected by a decrease of the reaction temperature and by an increase of the total pressure (cf. entries 17–20 and 16–17). Addition of a three-fold excess of free ligand also showed a beneficial effect on the formation of the branched isomer which at 25 °C accounted for 96% of the reaction product and did not change upon further addition of free ligand up to a ratio of 15:1. This is one of the most favorable branched selectivities recorded in the hydroformylation of styrene with a rhodium catalyst containing a chiral ligand.

Using enantiopure *R*-Me_2binas as the ligand, preferential formation of (*S*)-2-phenylpropanal was observed. High temperatures, high pressures and excess of free ligand all favored an improvement of the stereoselectivity. The effect of the last variable was particularly pronounced since the *e.e.* was almost doubled after addition of 3 mol of free ligand (cf. entries 14–16 and 15–17). The enantioselectivities, however, were quite low and did not exceed 15% *e.e.* in the best run. It is important to note that, when using the dithioether ligand, a new stereogenic center is formed when the sulfur ligand is bonded to the rhodium central atom. However, the presence of different diastereoisomeric species was not observed in NMR experiments, even those performed at low temperatures.

The *e.e.* value was increased up to 20% upon introduction on sulfur of i-propyl groups in place of methyl groups (entry 31). As for the rest, the general behavior of the Rh-complex with the i-propyl-substituted ligand was completely comparable with the one containing Me_2binas.

As a general trend, the complexes with the biphes-derived thioethers displayed comparable chemo- and regio-selectivities and a slightly higher catalytic activity than the corresponding binas-based counterparts (Table 4). Stereoselectivity was, however, the most significant difference between the two sets of catalysts. With Me_2biphes-derived ligands the *e.e.*s were consistently lower than with the corresponding Me_2binas derivatives and close to zero. With iPr_2biphes the hydroformylation was completely devoid of stereoselectivity and the branched aldehyde was always racemic. In all other respects the two biphes thioethers were quite similar.

As the sulfur in thioethers is considered to be a fairly weak donor, one may wonder if it could be easily displaced from the coordination sphere of the metal when a stronger donor competing for the metal is present in significant concentration.

Actually, we observed that when triphenylphosphine is added as a co-ligand, the reaction is no more stereoselective, regardless of the thioether ligand. The branched selectivity, moreover, is not the same as the one obtained in the same reaction without PPh_3, and it is almost identical to one recorded in a blank reaction with $[Rh(cod)_2]ClO_4/PPh_3$ as the in situ catalyst. This fact suggests that PPh_3 is able to displace completely the chelate thioether form coordination to rhodium and that in this case the actual hydroformylation catalyst is $[RhH(CO)_x(PPh_3)_y]$. Furthermore, the reactivity of $[Rh(cod)(dithioether)]^+$ towards triphenylphosphine has been studied and the displacement of the dithioether has been observed.

Increasing CO concentrations may be expected to exert the same effect on alkyl thioether complexes. Our experiments, however, do not support this hypothesis. In fact, competitive experiments, where $[Rh(cod)_2]ClO_4$ in the presence of a thioether ligand were employed as in situ catalysts, resulted in quite different catalytic activity and regioselectivity. Additionally, as a general trend, the stereoselectivity of thioether-derived catalysts increased upon increasing the CO pressure. These results support the view that chelate thioether sulfur donors are not displaced by carbon monoxide even when it is present in high concentrations.

In summary, these results point out that the axially chiral biphes structure is not more efficient than the less expanded binas and that atropisomeric sulfur donor ligands, although providing high efficient hydroformylation catalysts, are not the most appropriate chiral inducers for this process.

3. Experimental

All syntheses of rhodium complexes were performed using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. The complexes $[\{M(\mu\text{-OMe})(cod)\}_2]$ (M = Rh, Ir), $[Rh(cod)_2]ClO_4$ and the ligands 1,1′-binaphthalene-2,2′-dithiol, 4,4′-biphenanthrene-3,3′-dithiol were prepared using literature methods [17,18,9]. Phosphorus reactants were of commercial origin and used without further purification. Tris(*o-tert*-(butylphenyl)phosphite was prepared as previously described [19]. All other reagents were commercial samples and were used as-purchased. Infrared spectra (KBr pellets or solution) were obtained using a Nicolet 5ZDX spectrophotometer. Elemental analyses were performed on a Carlo Erba microanalyzer. ^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz spectrophotometer, chemical shifts being quoted in parts per million downfield from internal $SiMe_4$. ^{31}P NMR spectra were obtained on the same equipment, using external H_3PO_4 as reference. Gas chromatographic analyses were carried out on a Hewlett-Packard Model 5890, a gas chromatograph with flame ionization detector using a 25 m capillary column (Ultra 2). Enantiomeric excesses were measured by GC on the same equipment using a 50 m capillary column (FS-Cyclodex β-I/P). Hydroformylation experiments were carried out in an autoclave with magnetic stirring.

3.1. Standard catalysis experiment

A solution of the substrate (20 mmol), the catalyst precursor (0.1 mmol) and the phosphorus compound in 15 ml of the anhydrous tetrahydrofuran were introduced into the evacuated autoclave. The gas mixture was introduced and the system was heated. When thermal equilibrium was reached, stirring was initiated. After the reaction time, the autoclave was cooled to room temperature and depressurized. Conversion and regioselectivities were determined by GC analysis of crude samples without the addition of any external standard. Enantiomeric excesses were measured by GC with a chiral column on the alcohols obtained by reduction of the product aldehydes.

4. Preparations

4.1. [(Rh$_2$(μ-biphes)(cod)$_2$)n] (n = 2 5, n = 1 6)

The compound H_2biphes (52.6 mg, 0.126 mmol) was added to a solution of [{Rh(μ-OMe)(cod)}$_2$] (60 mg, 0.124 mmol) in dichloromethane. The yellow solution became red. After stirring at room temperature for 10 min, methanol was added to give an orange precipitate of [{Rh$_2$(μ-biphes)(cod)$_2$}$_2$] **5** which was filtered off and dried in vacuo (72.8 mg, 70% yield). (Found: C, 64.7; H, 4.5; S, 7.8. Calc. for $C_{44}H_{40}Rh_2S_2$: C, 63.0; H, 4.8; S, 7.6.) NMR ($CDCl_3$): ^{1}H, δ 8.20 (d, 2H, J = 8.25 Hz, ArH); 7.80 (d, 2H, J = 8.34 Hz, ArH); 7.51 (d, 2H, J = 8.58 Hz, ArH); 7.32 (d, 2H, J = 7.98 Hz, ArH); 7.29 (d, 2H, J = 8.49 Hz, ArH), 6.98 (t, 2H, J = 7.38 Hz, ArH); 6.61 (t, 2H, J = 7.05 Hz, ArH); 5.95 (d, 2H, J = 8.79 Hz, ArH); 4.49 (br, m, 4H, CH cod); 4.15 (br, m, 4H, CH cod); 2.21 (br, m, 8H, CH_2 cod); ^{13}C{^{1}H}, δ 133.6, 127.6, 126.6, 126.5, 126.2, 126.1, 125.1, 124.3 (Ar); 78.9 (CH cod); 79.3 (CH, cod); 33.3 (CH_2 cod); 29.4 (CH_2 cod). M_r 1677.4 (1547 by osmometry in CH_2Cl_2 at 25 °C).

After separating of the orange complex, the solvent of the resulting solution was evaporated under reduced pressure to 3 cm^3. After cooling the flask in ice the red product [Rh$_2$(μ-biphes)(cod)$_2$] **6** was obtained, filtered off, washed with methanol and vacuum dried (23.0 mg, 22% yield). X-ray-quality crystals were grown by cooling to −20 °C a dichloromethane solution of **6**.

4.2. [{Ir$_2$(μ-biphes)(cod)$_2$}n] · nCH$_2$Cl$_2$ 7

The ligand H_2biphes (19.0 mg, 0.045 mmol) was added to a solution of [{Ir(μ-OMe)(cod)}$_2$] (30 mg, 0.045 mmol) in dichloromethane. The yellow solution became red. After stirring at room temperature for 10 min, methanol was added to give a dark red precipitate of [{Ir$_2$(μ-biphes)(cod)$_2$}$_n$] · nCH$_2$Cl$_2$ **7** which was filtered off and dried in vacuo (29.8 mg, 65% yield). (Found: C, 49.8; H, 3.9; S, 5.4. Calc. for $C_{45}H_{42}Cl_2Ir_2S_2$: C, 49.0; H, 3.8; S, 5.8.) NMR ($CDCl_3$): ^{1}H, δ 7.68 (d, 2H, J = 8.15 Hz, ArH); 7.48 (d, 2H, J = 7.51 Hz, ArH); 7.26 (d, 2H, J = 8.12 Hz, ArH); 7.26 (m, 4H, ArH); 7.19 (m, 2H, ArH), 7.00 (m, 2H, ArH); 6.79 (m, 4H, ArH); 4.21 (m, 4H, CH cod); 2.00 (m, 8H, CH_2 cod); 1.83 (m, 8H, CH_2 cod); ^{13}C{^{1}H}, δ 133.1, 130.2, 127.3, 126.7, 126.2, 125.5, 125.4, 124.1 (Ar); 68.3 (CH cod); 66.4 (CH, cod); 34.0 (CH_2 cod); 30.9 (CH_2 cod).

4.3. [Ir$_2$(μ-binas)(cod)$_2$] 8

The compound H_2binas (29.0 mg, 0.09 mmol) was added to a solution of [{Ir(μ-OMe)(cod)}$_2$] (60 mg, 0.09 mmol) in dichloromethane. The yellow solution became red. After stirring at room temperature for 10 min, the resulting solution was evaporated under reduced pressure to 3 cm^3. After cooling the flask in ice, addition of methanol gave the dark red solid [Ir$_2$(μ-binas)(cod)$_2$] **8** which was then filtered off, washed with methanol and vacuum dried (52.1 mg, 63% yield). (Found: C, 46.9; H, 3.8; S, 6.9. Calc. for $C_{36}H_{36}Ir_2S_2$: C, 47.1, H, 3.9, S, 7.0.) NMR ($CDCl_3$): ^{1}H, δ 7.64 (d, 2H, J = 7.77 Hz, ArH); 7.49 (d, 2H, J = 8.79 Hz, ArH); 7.39 (d, 2H, J = 8.79 Hz, ArH); 7.18 (t, 2H, J = 7.77 Hz, ArH); 6.99 (t, 2H, J = 7.92 Hz, ArH), 6.52 (d, 2H, J = 8.43 Hz, ArH); 4.06 (m, 4H, CH cod); 3.55 (m, 4H, CH cod); 1.98 (m, 8H, CH_2 cod); 1.79 (m, 8H, CH_2 cod); ^{13}C{^{1}H}, δ 130.1, 129.2, 127.4, 127.0, 125.5, 124.5 (Ar); 67.0 (CH cod); 65.0 (CH, cod); 33.8 (CH_2 cod); 31.0 (CH_2 cod).

4.4. [Rh$_2$(μ-biphes)(CO)$_4$] 9

Carbon monoxide was bubbled through a solution of {Rh$_2$(μ-biphes)(cod)$_2$}$_n$] (n = 1,2) (60 mg, 0.072 mmol (n = 1); 0.036 mmol (n = 2)) in dichloromethane for 10 min. The initial red solution darkened. Adding methanol gave a dark red precipitate which was filtered off, washed with methanol and dried in vacuo (51 mg, 97% yield). (Found: C, 52.0; H, 2.4, S, 7.2. Calc. for $C_{32}H_{16}O_4Rh_2S_2$: C, 52.3; H, 2.2; S, 8.7.) NMR ($CDCl_3$): ^{1}H, δ 8.1–6.5 (br, ArH); ^{13}C{^{1}H}, δ 185–182 (CO), 131–125 (Ar); IR (KBr): 2074m, 2058s and 2009s, (CH_2Cl_2): 2076m, 2061s and 2014s cm^{-1}. M_r 734.4 (891 by osmometry in CH_2Cl_2 at 25 °C).

4.5. [{Rh$_2$(μ-biphes)(CO)$_2$(PPh$_3$)$_2$}$_2$] · 2CH$_2$Cl$_2$ 10

Slightly more (10%) than the stoichiometric amount of triphenylphosphine (47 mg, 0.18 mmol) was added to a solution of [Rh$_2$(μ-biphes)(CO)$_4$ (60 mg, 0.08 mmol) in dichloromethane (5 cm^3). The resulting solution was stirred for 10 min, filtered off and the filtrate reduced to

0.5 cm^3 under vacuum. Addition of 5 cm^3 of methanol caused precipitation of a brown solid which was filtered off, washed with cold methanol and dried under vacuum (81.8 mg, 85% yield). (Found: C, 62.7; H, 3.8; S, 5.0. Calc. for $C_{67}H_{48}Cl_2O_2P_2Rh_2S_2$: C, 62.5; H, 3.7; S, 5.0.) NMR ($CDCl_3$): $^{31}P\{^1H\}$, δ 45.4 (d, J_{P-Rh} = 174 Hz); IR (KBr): 1975s; (CH_2Cl_2): 1979s cm^{-1}. M_r 2406 (2231 by osmometry in CH_2Cl_2 at 25 °C).

4.6. $[\{Rh_2(\mu\text{-biphes})(CO)_2[P(C_6H_{11})_3]_2\}_2] \cdot CH_2Cl_2$ 11

Slightly more (10%) than the stoichiometric amount of tricyclohexylphosphine (50.4 mg, 0.18 mmol) was added to a solution of $[Rh_2(\mu\text{-biphes})(CO)_4]$ (60 mg, 0.08 mmol) in dichloromethane (5 cm^3). The resulting solution was stirred for 20 min, filtered off and the filtrate reduced to 0.5 cm^3 under vacuum. Addition of 5 cm^3 of methanol caused precipitation of a brown solid which was collected by filtration, washed with cold methanol and dried under vacuum (89.0 mg, 90% yield). (Found: C, 62.6; H, 6.5; S, 4.9. Calc. for $C_{66.5}H_{83}ClO_2P_2Rh_2S_2$: C, 62.8; H, 6.5; S, 5.0.) NMR ($CDCl_3$): $^{31}P\{^1H\}$, δ 35.52 (d, J_{P-Rh} = 124 Hz), 36.98 (d, J_{P-Rh} = 118 Hz); IR (KBr): 1992s, 1963m and 1948m; (CH_2Cl_2): 1992m, 1964m and 1949s cm^{-1}. M_r 2477 (2342 by osmometry in CH_2Cl_2 at 25 °C).

4.7. $[\{Rh_2(\mu\text{-biphes})(CO)_3[P\text{-}(OC_6H_4Bu^t\text{-}o)_3]\}_2] \cdot CH_2Cl_2$ 12

Tris(*o-tert*-butyl-phenyl)phosphite) (43 mg, 0.09 mmol) was added to a solution of $[Rh_2(\mu\text{-biphes})(CO)_4]$ (30 mg, 0.04 mmol) in dichloromethane (5 cm^3) at a P:Rh ratio of 5:1. The resulting solution was stirred for 30 min, filtered off and the filtrate reduced to 0.5 cm^3 under vacuum. Addition of 5 cm^3 of methanol caused precipitation of a brown solid which was filtered off, washed with cold methanol and dried under vacuum (42.1 mg, 88.6% yield). (Found: C, 60.3; H, 4.6; S, 5.5. Calc. for $C_{615}H_{56}ClO_6PRh_2S_2$: C, 60.2; H, 4.6; S, 5.2.) NMR (C_6D_6): $^{31}P\{^1H\}$ δ 119 (br); IR (KBr); 2075m, 2059s and 2007s; (CH_2Cl_2); 2076m, 2060s and 2010s cm^{-1}.

4.8. $[Rh(cod)(Me_2biphes)]ClO_4 \cdot CH_2Cl_2$ 13

To a solution of $[Rh(cod)_2]ClO_4$ (40 mg, 0.096 mmol) in dichloromethane (5 cm^3) was added the stoichiometric amount of Me_2biphes (42.8 mg, 0.096 mmol). The orange solution became yellow. After stirring at room temperature for 10 min, methanol was added to give a yellow precipitate of **13** which was filtered off and dried under vacuum (64 mg, 88% yield). (Found: C, 54.2; H, 4.3; S, 7.8. Calc. for $C_{39}H_{36}Cl_3O_4RhS_2$: C, 55.4 H, 4.3; S, 7.8.) NMR ($CDCl_3$): ^1H, δ 8.10 (d, 2H, ArH); 7.85 (d, 2H, ArH); 7.83 (m, 2H, ArH); 7.80 (d, 2H, ArH); 7.77 (d, 2H, ArH); 7.65 (d, 2H, ArH); 7.33 (t, 2H, ArH); 6.86 (t, 2H, ArH); 4.22 (br, m, 4H, CH cod); 3.75 (br, m, 2H, CH cod); 2.50 (br, m, 4H, CH_2 cod); 2.24 (s, 3H, CH_3); 1.75 (br, m, 4H, CH_2 cod); $^{13}C\{^1H\}$, δ 133.5, 129.9, 128.6, 127.7, 127.1, 126.4, 126.2, 125.9, 125.6, 123.8 (Ar); 78.8 (CH cod); 78.6 (CH, cod); 30.9 (CH_2 cod); 16.1 (CH_3).

5. Crystallography

Suitable crystals of the complex **6** were grown from a dichloromethane solution cooled to −20 °C and mounted on a glass fiber.

5.1. Crystal data

Compound **6**: $Rh_2S_2C_{44}H_{40}$, M = 838.70, monoclinic, a = 10.95(6), b = 26.87(6), c = 12.68(6) Å, β = 103.12(6)°, U = 3633.3 $Å^3$, space group $P2_1/c$ (no. 14), Z = 4, D_c = 1.533 g cm^{-3}, $F(000)$ = 1704. Dark red, crystal dimensions 0.2 × 0.2 × 0.1 mm^3, μ(Mo Kα) = 10.54 cm^{-1}.

5.2. Data collection and processing

The data collection and processing were performed at room temperature on a Mar Research image plate scanner; graphite-monochromated Mo Kα radiation was used to measure 95 2° frames, 180 s per frame.

5.3. Structure analysis and refinement

The XDS package was used to give 5842 unique reflections (merging R = 0.0587). The heavy atoms were found from the Patterson map using the SHELX86 program [20] and refined subsequently from successive difference Fourier maps using SHELXL [21] by full-matrix least squares of 515 variables, to a final R-factor of 0.065 for 5713 reflections with $[F_o] > 4\sigma(F_o)$. All atoms were revealed by the Fourier map difference. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically, cod hydrogen atoms were refined with a fixed isotropic atomic displacement parameter and the aromatic ones were refined isotropically. R values: R_1 = 0.0652 ($[F_o] > 4\sigma(F_o)$, for 5713 reflections); R_2 = 0.0867 (all data). The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0276 \times P)^2 + 28.38 \times P]$ where $P = [\mathrm{Max}(F_o^2 + 2F_c^2)/3]$ with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Largest difference peak and hole in the final difference map: 0.819 and −0.920 e^- $Å^{-3}$. Data collection parameters including R_1 ($[F_o] > 4\sigma(F_o)$) and R_2 (all data) values are summarized in Table 2. Additional material available from the Cambridge Crystallographic

Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Ministerio de Educación y Ciencia for financial support (Dirección General de Investigación Científica y Técnica, grants PB-91-0663-CO3-01 and SB92-AF0608948). A. Aaliti gratefully acknowledges the Ministère de l'Education Nationale du Maroc.

References

[1] (a) S. Gladiali, J.C. Bayón, C. Claver, Tetrahedron: Asymmetry 6 (1995) 1453. (b) F. Agbossou, J.F. Carpentier, A. Mortreux, Chem. Rev. 95 (1995) 2485.
[2] C. Botteghi, S. Paganelli, A. Schionato, M. Marchetti, Chirality 3 (1991) 355.
[3] (a) N. Sakai, S. Mano, K. Nozaki, H. Takaya, J. Am. Chem. Soc. 115 (1993) 7033. (b) N. Sakai, K. Nozaki, H. Takaya, J. Chem. Soc. Chem. Commun. (1994) 395. (c) T. Higashizima, N. Sakai, K. Nozaki, H. Takaya, Tetrahedron Lett. 35 (1994) 2023.
[4] (a) G.J.H. Buisman, E.J. Vos, P.C.J. Kamer, P.W.N.M. van Leeuwen, Tetrahedron: Asymmetry 4 (1993) 1625. (b) J.E. Babin, G.T. Whiteker, WO 93/03839 US 911.518, 1992. (c) T.V. Rajan Babu, T.A. Ayers, Tetrahedron Lett. 35 (1994) 4295.
[5] Ph. Kalck, J.M. Frances P.M. Pfister, T.G. Southern, A. Thorez, J. Chem. Soc. Chem. Commun. (1983) 510.
[6] Ph. Kalck, in: A. de Meijere, H. Tom Dick (Eds.), Organometallics in Organic Syntheses, Springer, Hamburg, 1987, pp. 297–320.
[7] C. Claver, S. Castillón, N. Ruiz, G. Delogu, D. Fabbri, S. Gladiali, J. Chem. Soc. Chem. Commun. (1993) 1833.
[8] N. Ruiz, S. Castillón, A. Ruiz, C. Claver, A. Aaliti, A. Alvarez-Larena, F. Piniella, G. Germain, J. Chem. Soc. Dalton Trans. (1996) 969.
[9] A. Dore, D. Fabbri, S. Gladiali, G. Volle, Tetrahedron: Asymmetry 6 (1995) 779.
[10] M.A. Ciriano, J.J. Pérez-Torrente, F. Viguri, F.J. Lahoz, L.A. Oro, A. Tiripicchio, M. Tiripicchio-Camellini, J. Chem. Soc. Dalton Trans. (1990) 1493.
[11] J.J. Bonnet, Ph. Kalck, R. Poilblanc, Inorg. Chem. 16 (1977) 1514.
[12] A.M. Masdeu, A. Ruiz, S. Castillón, C. Claver, P.B. Hitchcock, P.A. Chaloner, C. Bo, J.M. Poblet, P. Sarasa, J. Chem. Soc. Dalton Trans. (1993) 2689.
[13] A. Elduque, L.A. Oro, M.T. Pinillos, A. Tiripicchio, F. Ugozzoli, J. Chem. Soc. Dalton Trans. (1994) 385.
[14] (a) Ph. Kalck, R. Poilblanc, Inorg. Chem. 14 (1975) 2779. (b) R. Choukroun, D. Gervais, J. Jaud, Ph. Kalck, F. Senocq, Organometallics, 5 (1986) 67. (c) C. Claver, Ph. Kalck, M. Ridmy, A. Thorez, L.A. Oro, M.T. Pinillos, M.C. Apreda, F.H. Cano, C. Foces-Foces, J. Chem. Soc. Dalton Trans. (1988) 1523.
[15] (a) J.C. Bayón, P. Esteban, J. Real, C. Claver, A. Ruiz, J. Chem. Soc. Chem. Commun. (1989) 1056. (b) A. Polo, J. Real, C. Claver, S. Castillón, J. Chem. Soc. Chem. Commun. (1990) 631. (c) A. Polo, C. Claver, S. Castillón, A. Ruiz, J.C. Bayón, J. Real, C. Mealli, D. Masi, Organometallics 11 (1992) 3525. (d) A. Polo, E. Fernández, C. Claver, S. Castillón, J. Chem. Soc. Chem. Commun. (1992) 639.
[16] A. Vizi-OrOsz, G. Pályi, L. Markó, J. Organomet. Chem. 57 (1973) 379.
[17] (a) R. Usón, L.A. Oro, J.A. Cabeza, Inorg. Synth. 23 (1985) 126. (b) J. Chatt, J.M. Davidson, J. Chem. Soc. A: (1965) 843. (c) R. Usón, L.A. Oro, F. Ibañez, Rev. Acad. Cien. Zaragoza 31 (1975) 169.
[18] (a) D.J. Cram, R.C. Hegelson, K. Koga, E.P. Kyba, K. Madan, L.R. Sousa, M.C. Siegel, P. Moreau, G.W. Gokel, J.M. Timko, D.Y. Sogah, J. Org. Chem. 43 (1978) 2758. (b) O. De Lucchi, G. Delogu, D. Fabbri, J. Org. Chem. 58 (1993) 1748.
[19] P.W.N.M. van Leeuwen, C.F. Roobeck, J. Organomet. Chem. 258 (1983) 343.
[20] G.M. Sheldrick, SHELXS 86, in: G.M. Sheldrick, C. Krüger, R. Goddard (Eds.), Crystallographic Computing, vol. 3, Oxford University Press, Oxford, 1985, p. 175.
[21] G.M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1993.