ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 586 (1999) 247–253

Journal of Organometallic Chemistry

Influence of the presence of heteroatoms in the olefin chain on the Pauson–Khand reaction with metal (Cr, W) carbene enyne complexes

Joan Pares [a], Josep M. Moretó [a], Susagna Ricart [a,*], José Barluenga [b,1], Francisco J. Fañanás [b]

[a] *Departament de Química Orgànica i Biológica, Institut d'Investigacions Químiques i Ambientals de Barcelona Josep Pascual Vila, (CSIC) C/J.Girona 18-26, E-08034 Barcelona, Spain*

[b] *Instituto Universitario de Química Organometalica Enrique Moles, Unidad Asociada al CSIC, Universidad de Oviedo, Julián Claveria 8, E-33011 Oviedo, Spain*

Received 7 April 1999

Abstract

The study of the influence caused by the presence of an heteroatom, either at an internal or terminal site of the olefin, on the outcome of the Pauson–Khand cycloaddition in metal carbene enyne complexes is reported. In this study the steric and electronic effects have been evaluated. A diversion from the normal course of the reaction mechanism is observed.

Keywords: Carbene complexes; Pauson–Khand cycloadditions; Steric effects; Electronic effects

1. Introduction

The presence of a transition metal amino carbene moiety adjacent to a triple bond has been found to facilitate the intramolecular cobalt mediated Pauson–Khand (P–K) cycloaddition [1]. Moreover, it allows, in some cases, the isolation of an intermediate corresponding to the stage immediately preceding the final reductive elimination (when all the C–C bonds but one have already been accomplished) [2]. Modifications on the enyne chain seem to be a good way to gain insight into the reaction mechanism and, in addition, by altering the electronic and/or steric features to achieve a higher reaction stereoselectivity.

As has been shown by Krafft and Juliano [3], the presence of coordinating heteroatoms in the starting organic enyne in the intramolecular reaction not only promotes the carbonylative cycloaddition but also enhances the resulting stereoselectivity. The presence of the amino group, in the case of metal carbene complexes, is essential for the cycloaddition to be accomplished, but we wondered about the possible effects of the presence of other (coordinating or not) heteroatoms on the allylic chain either in the product distribution or in the trapping of intermediates.

A previous study related to the synthesis of different heteroatom substituted allyl amino derivatives [4] allowed us to obtain heteroatom substituted metal carbene enynes by means of their reaction with the carbene functionality by low temperature aminolysis of the corresponding alkoxycarbenes.

2. Results

2.1. Aminolysis reaction

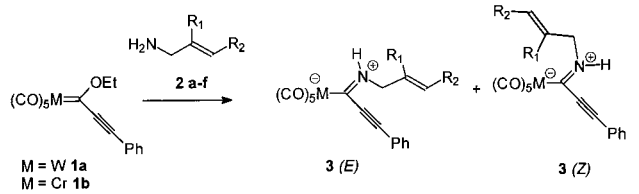
Eight new allylamino carbene complexes displaying differences in heteroatoms and their site in the allylic chain were synthesized in generally good yields, as is shown in Table 1. Only with two amines were the yields

* Corresponding author. Tel.: +34-93-4006115; fax: +34-93-2045904.

E-mail address: srmqob@cid.csic.es (S. Ricart)

[1] Also corresponding author.

0022-328X/99/$ - see front matter
PII: S0022-328X(99)00287-9



rather low (entries 2, 3 and 8, Table 1): in the first case this could be justified by the steric hindrance brought about by the presence of the thiobenzyl unit on the starting amine; in the second the neutralization of the corresponding amine hydrochloride in the presence of a hydroxyl group might have caused solubility problems.

In all cases the only product obtained corresponded to the one with the allyl chain in *trans* arrangement to the metal center (isomer *E*) [5]. The corresponding *Z* isomer could be detected in some cases in the reaction mixture but always in very low quantities ($< 3\%$ of the overall yield).

2.2. Reaction with $Co_2(CO)_8$

The cobalt carbonyl mediated cycloaddition (P–K reaction) was tried with aminocarbene complexes **3** obtained as above. The results are gathered in Table 2.

From Table 2 we can observe that although the cyclopentenone adduct **6** was obtained in all cases, the presence of a heteroatom such as sulfur, in the internal sp^2 carbon atom of the allylic chain, produces a global lowering in the final yields when compared with the corresponding unsubstituted allylic carbene complexes. Moreover, in the case of benzyl thio derivatives (entries 2 and 3) an isomerization of the allylic chain (from *E* to *Z* position regarding the metal pentacarbonyl moiety) [6] provided the formation of the tetracarbonyl adducts (**5b**, **5c**), pointing out the importance of steric hindrance in these reactions as reported in a previous paper [2b]. No further reaction beyond this tetracarbonyl species could be recorded.

In the case of silicon and tin substituted allylic substrates (**3f**, **3g**) a common cyclopentenone adduct **6f** (Table 2, entries 4 and 5) was obtained that would arise most probably from the lability of the trimetylsilyl and tributylstannil groups, respectively, possibly enhanced by the stabilization of an adjacent α-keto carbanion derived from the final cycloadduct.

In entry 6 (Table 2) we obtained a mixture (3:1) of the corresponding diastereomers **6h**. At present we have no good explanation for the lack of stereochemical control when starting from allyl systems with a *cis* double bond, but we cannot exclude the possibility of a previous isomerization of the allylic double bond before the P–K cyclization is accomplished. From the reaction of crotylamino carbene complexes, good stereoisomeric control was obtained for the *trans* double bond, but the same mixture of diastereomers was obtained from the *cis* isomer [2]. The presence of the heteroatom (oxygen) in the substituent of the double bond apparently would not introduce any change in the reaction rates and therefore in the product distribution of the mixture obtained.

2.3. Reaction with aminocarbenes *3d* and *3e*

The aminocarbenes **3d** and **3e** displayed an absolutely different behavior under the same reaction conditions. When the $Co_2(CO)_8$ was added to a THF solution of these compounds no cyclopentenone adduct was obtained. Instead, a new set of carbene complexes **7** and **8** was identified in both cases (Scheme 1).

These diene complexes seem to arise from a diversion from the normal course of the P–K cycloaddition after the first insertion has been accomplished. Prior to the final carbonylation formal hydride transfer and decoordination would be the preferred pathways to release the cobalt moiety. A similar mechanism was already described by Pauson [7] and Krafft [8] in the P–K reaction of alkenes bearing an electron-withdrawing substituent.

Table 1
Preparation of alkynyl aminocarbene complexes **3** from complexes **1** and allylamines **2** [a]

	Starting carbene	Amine	R_1	R_2	Yield (%) [b]
1	**1a**	**2a**	SCH_3	H	**3a** (92)
2	**1a**	**2b**	SCH_2Ph	H	**3b** (44)
3	**1b**	**2b**	SCH_2Ph	H	**3c** (52)
4	**1a**	**2c**	H	SCH_3	**3d** (74)
5	**1b**	**2c**	H	SCH_3	**3e** (60)
6	**1a**	**2d**	H	$Si(CH_3)_3$	**3f** (93)
7	**1a**	**2e**	H	$SnBu_3$	**3g** (92)
8	**1a**	**2f** [c]	H	CH_2OH	**3h** (20) [b]

[a] Standard reaction conditions, THF, −78°C.
[b] Based on starting carbene **1**.
[c] Starting from the corresponding hydrochloride.

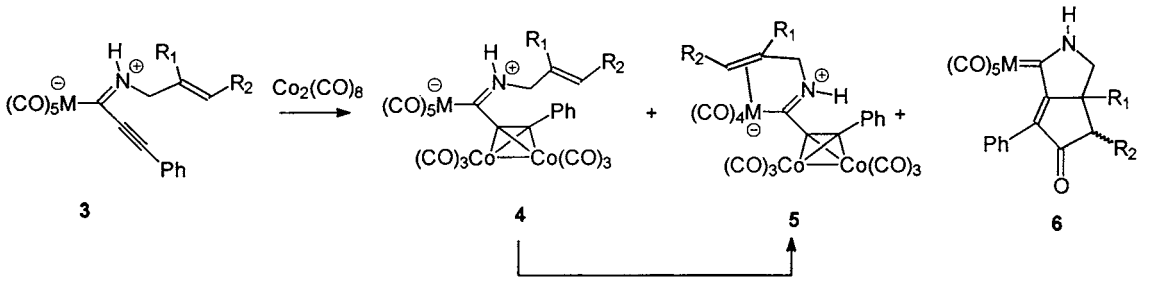


Table 2
Reaction of alkynyl aminocarbene complexes **3** with $Co_2(CO)_8$ to give compounds **4**, **5** and **6** [a]

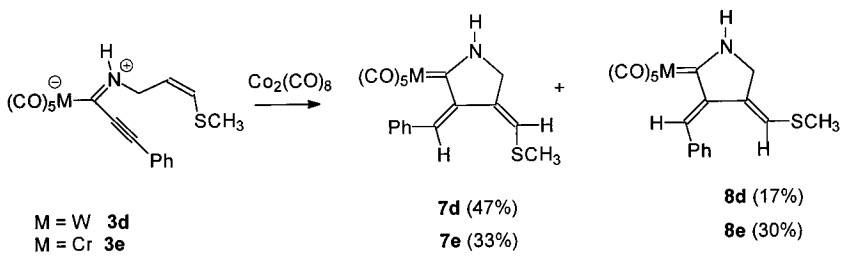
	Starting compound		Yields [b] (%)	
1	**3a**	**4a** (21)	**5a** (trc.)	**6a** (13)
2	**3b**	**4b** (trc.)	**5b** (5)	**6b** (26)
3	**3c**	**4c** (trc.)	**5c** (18)	**6c** (24)
4	**3f**	–	–	**6f** (56) [c]
5	**3g**	–	–	**6f** (41)
6	**3h**	–	–	**6h** (50) [d]

[a] Standard reaction conditions: $Co_2(CO)_8$ (1.1 equivalents), THF, r.t.
[b] Based on starting compounds **3**.
[c] **6f** $R_1 = R_2 = H$.
[d] Obtained as a mixture (3/1, *cis*/*trans*) of diastereomers.

In our case we suppose that the presence of the sulfur center blocks the carbonylation step allowing alternative (β-elimination) processes to take place.

A ^{1}H-NMR study of compounds **7d** and **8d** led us to assign unequivocally all the protons of the double bonds. The stereochemistry of compounds **7** and **8** was established by means of nOe measurements as is shown in Fig. 1.

No allylic coupling was observed in these systems but only a slight broadening of the singlets corresponding to the vinyl protons (at 6.27 and 6.63 ppm, respectively for compounds **7d** and **8d**).



Scheme 1.

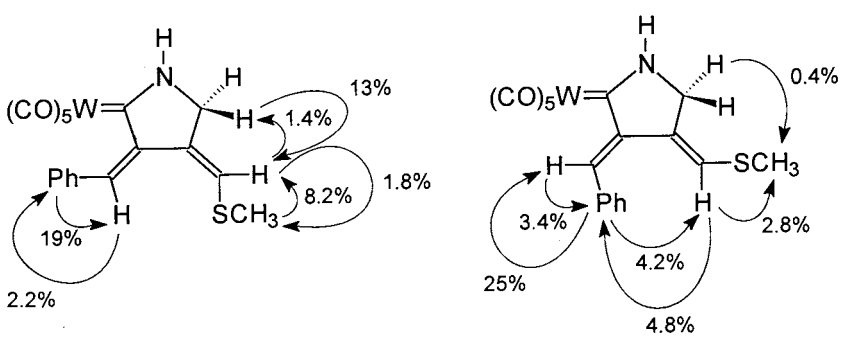


Fig. 1.

3. Conclusions

The results obtained with heterosubstituted allyl amino carbene complexes confirm the importance of the steric and coordinative effects in the P–K reaction mediated by metal carbene complexes already pointed elsewhere.

The formation of compounds **7** and **8** indicates that the presence of a heteroatom with coordinative properties can not only stabilize the cobalt intermediates as shown by Krafft in intramolecular systems, but also lead to a diversion of the normal course of the mechanism by a complete inhibition of the carbonyl insertion step.

4. Experimental

Unless otherwise stated all common reagents and solvents were used as obtained from commercial suppliers without further purification.

NMR spectra were recorded on a Varian Gemini-200 (200 MHz for ^{1}H-NMR and 50 MHz for ^{13}C) or a Varian XL-300 apparatus (300 MHz for ^{1}H-NMR and 75.4 MHz for ^{13}C). All samples of carbene complexes were filtered through a pad of Celite and EDTA prior to recording the spectra. IR spectra were recorded on a Bomem FT-IR M-120 spectrophotometer. Mass spectra were obtained on an AutoSpec-Q mass spectrometer. Elemental analyses were performed using a Carlo Erba 1106 apparatus.

Flash column chromatography was performed with 'flash grade' silica (SDS 230–400 mesh).

Unless otherwise indicated all the reactions were performed under Ar atmosphere.

Carbene complexes **1a**,**b** [9] were prepared by literature procedures and yields of final products were not optimized.

4.1. General procedure for aminolysis. Preparation of the aminocarbene complex *3a*

A total of 0.155 g of the corresponding allyl amine **2a** (1.5 mmol) were added over a stirred solution of 0.723 g of the alkoxy alkynyl carbene complex **1a** (1.5 mmol) in 20 ml of dry THF at -70°C. The reaction course was monitored by thin-layer chromatography (4:1 hexane–CH_2Cl_2). After the starting product had completely reacted, the solvent was removed and the residue passed through a flash chromatography column using the mentioned eluent, affording 0.744 g (92% yield) of the amino complex **3a** as an orange solid.

3a. IR ($CHCl_3$): 3381, 2167, 2063, 1974, 1938 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.16 (s, 3H, SCH_3), 4.27 (d, $J = 5.8$ Hz, 2H, NCH_2), 4.78 (d, $J = 1$ Hz, 1H, CH_2), 5.18 (d, $J = 1$ Hz, 1H, CH_2), 7.21–7.46 (m, 5H, Ph), 8.62 (bs, 1H, NH). ^{13}C-NMR ($CDCl_3$): δ 14.6 (q), 57.2 (t), 91.5 (s), 108.8 (t), 121.3 (s), 128.6 (s), 128.7 (d), 130.8 (d), 132.4 (d), 140.7 (s), 198.2 (s), 203.7 (s), 233.8 (C = W). Anal. Calc. for $C_{18}H_{13}O_5NSW$: C, 40.07; H, 2.41; N, 2.59; S, 5.93. Found: C, 40.15; H, 2.41; N, 2.59; S, 5.75%.

4.2. Preparation of the aminocarbene complex *3b*

According to the general procedure 0.482 g (1 mmol) of complex **1a** were allowed to react with 0.260 g (1 mmol) of allylamine **2b**. After purification by flash chromatography 0.270 g (44% yield) of the corresponding aminocarbene **3b** were obtained as an orange solid.

3b. IR ($CHCl_3$): 3375, 2167, 2061, 1974, 1920 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 4.02 (s, 2H, SCH_2), 4.38 (d, $J = 5.8$ Hz, 2H, NCH_2), 5.15 (s, 1H, CH_2), 5.38 (s, 1H, CH_2), 7.25–7.57 (m, 10H, Ph), 8.70 (bs, 1H, NH). ^{13}C-NMR ($CDCl_3$): δ 36.7 (t), 57.2 (t), 91.7 (s), 112.9 (t), 121.4 (s), 127.7 (d), 128.8 (d), 131.0 (d), 132.4 (s), 132.5 (d), 135.8 (s), 139.0 (s), 198.3 (s), 203.7 (s), 234.2 (C = W). Anal. Calc. for $C_{24}H_{17}O_5NSW$: C, 46.82; H, 2.76; N, 2.26; S, 5.20. Found: C, 46.61; H, 2.76; N, 2.24; S, 5.17%.

4.3. Preparation of the aminocarbene complex *3c*

According to the general procedure 0.700 g (2 mmol) of complex **1b** were allowed to react with 0.358 g (2 mmol) of allylamine **2b**. After purification by flash chromatography 0.495 g (52% yield) of the corresponding aminocarbene **3c** were obtained as an orange solid.

3c. IR ($CHCl_3$): 3375, 2165, 2056, 1980, 1942 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 4.03 (s, 2H, SCH_2), 4.47 (s, 2H, NCH_2), 5.17 (s, 1H, CH_2), 5.40 (s, 1H, CH_2), 7.38–7.57 (m, 10H, Ph), 8.85 (bs, 1H, NH). ^{13}C-NMR ($CDCl_3$): δ 36.5 (t), 57.1 (t), 89.1 (s), 112.6 (t), 121.4 (s), 127.5 (d), 128.6 (d), 130.8 (d), 132.1 (s), 132.4 (d), 135.4 (s), 139.3 (s), 217.0 (s), 223.1 (s), 257.7 (C = W). Anal. Calc. for $C_{24}H_{17}O_5NSCr$: C, 59.62; H, 3.52; N, 2.89; S, 6.62. Found: C, 59.54; H, 3.60; N, 2.85; S, 6.67%.

4.4. Preparation of the aminocarbene complex *3d*

According to the general procedure 0.723 g (1.5 mmol) of complex **1a** were allowed to react with 0.155 g (1.5 mmol) of allylamine **2c**. After purification by flash chromatography 0.600 g (74% yield) of the corresponding aminocarbene **3d** were obtained as an orange solid.

3d. IR ($CHCl_3$): 3379, 2167, 2061, 1974, 1936 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.18 (s, 3H, CH_3), 4.17 (td, $J =$ 5.8, 1 Hz, 2H, NCH_2), 5.45 (dt, $J = 9.4$, 6.6 Hz, 1H,

SC*H*), 6.12 (d, $J = 9.4$ Hz, 1H, C*H*), 7.42–7.58 (m, 5H, Ph), 8.46 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 17.2 (q), 50.7 (t), 91.5 (s), 119.5 (d), 121.4 (s), 128.4 (s), 128.7 (d), 130.8 (d), 132.4 (s), 134.3 (d), 198.3 (s), 203.6 (s), 232.1 (C = W). Anal. Calc. for $C_{18}H_{13}O_5NSW$: C, 40.07; H, 2.41; N, 2.59; S, 5.93. Found: C, 40.24; H, 2.39; N, 2.68; S, 5.88%.

4.5. Preparation of the aminocarbene complex *3e*

According to the general procedure 0.700 g (2 mmol) of complex **1b** were allowed to react with 0.210 g (2 mmol) of allylamine **2c**. After purification by flash chromatography 0.480 g (60% yield) of the corresponding aminocarbene **3e** were obtained as an orange solid.

3e. IR ($CHCl_3$): 3375, 2167, 2056, 1978, 1942 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.34 (s, 3H, CH_3), 4.46 (m, 2H, NCH_2), 5.65 (m, 1H, SC*H*), 6.32 (d, $J = 9$. Hz, 1H, C*H*), 7.44–7.57 (m, 5H, Ph), 8.83 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 17.1 (q), 50.9 (t), 89.1 (s), 119.7 (d), 121.5 (s), 128.6 (s), 130.6 (d), 132.0 (d), 132.1 (s), 134.0 (d), 217.0 (s), 223.5 (s), 255.1 (C = Cr). Anal. Calc. for $C_{18}H_{13}O_5NSCr$: C, 53.07; H, 3.19; N, 3.44; S, 7.86. Found: C, 53.02; H, 3.17; N, 3.44; S, 7.82%.

4.6. Preparation of the aminocarbene complex *3f*

According to the general procedure 0.723 g (1.5 mmol) of complex **1a** were allowed to react with 0.193 g (1.5 mmol) of allylamine **2d**. After purification by flash chromatography 0.794 g (93% yield) of the corresponding aminocarbene **3f** were obtained as an orange solid.

3f. IR ($CHCl_3$): 3379, 2167, 2063, 1974, 1938 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.26 (s, 9H, CH_3), 4.41 (td, $J =$ 6.6, 1.1 Hz, 2H, NCH_2), 6.03 (d, $J = 14$ Hz, 1H, SiC*H*), 6.42 (dt, $J = 14$, 6.6 Hz, 1H, C*H*), 7.40–7.63 (m, 5H, Ph), 8.61 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 0.10 (q), 54.3 (t), 91.5 (s), 121.3 (s), 128.5 (s), 128.7 (d), 130.8 (d), 132.2 (d), 137.4 (d), 138.7 (d), 198.3 (s), 203.6 (s), 231.9 (C = W). Anal. Calc. for $C_{20}H_{19}O_5NSiW$: C, 42.48; H, 3.36; N, 2.48. Found: C, 42.50; H, 3.31; N, 2.46%.

4.7. Preparation of the aminocarbene complex *3g*

According to the general procedure 0.723 g (1.5 mmol) of complex **1a** were allowed to react with 0.518 g (1.5 mmol) of allylamine **2e**. After purification by flash chromatography 1.09 g (92% yield) of the corresponding aminocarbene **3g** were obtained as an orange solid.

3g. IR ($CHCl_3$): 3377, 2165, 2063, 1974, 1940 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.90 (t, $J = 7.2$ Hz, 9H, CH_3), 0.98–1.04 (m, 6H, SnCH_2), 1.30–1.37 (m, 6H, CH_2), 1.48–1.56 (m, 6H, CH_2), 4.26 (t, $J = 6$ Hz, 2H, NCH_2), 6.41 (d, $J = 12.3$ Hz, 1H, SnC*H*), 6.66 (dt, $J = 12.3$, 6 Hz, 1H, C*H*), 7.40–7.58 (m, 5H, Ph), 8.47 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 10.4 (t), 13.6 (q), 27.2 (t), 29.0 (t), 57.6 (t), 91.7 (s), 121.4 (s), 128.5 (s), 128.7 (d), 130.8 (d), 132.3 (d), 138.9 (d), 139.4 (d), 198.3 (s), 203.5 (s), 232.1 (C = W). Anal. Calc. for $C_{29}H_{37}O_5NSnW$: C, 44.56; H, 4.73; N, 1.80. Found: C, 44.60; H, 5.01; N, 1.96%.

4.8. Preparation of the aminocarbene complex *3h*

According to the general procedure 0.482 g (1 mmol) of complex **1a** were allowed to react with a mixture of 0.307 g (1 mmol) of the allylamine **2f** hydrochloride and 0.252 g (2.5 mmol) of triethylamine. After purification by flash chromatography 0.095 g (18% yield) of the corresponding aminocarbene **3h** were obtained as an orange solid.

3h. IR ($CHCl_3$): 3375, 2950, 2358, 2165, 2061, 1973, 1932 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 4.34–4.31 (m, 4H, NCH_2, CH_2OH), 5.76 (tt, $J = 11.1$, 6.9, Hz, 1H, C*H*), 5.96 (tt, $J = 11.1$, 6 Hz, 1H, C*H*), 7.35–7.56 (m, 5H, Ph), 9.20 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 49.7 (t), 58.6 (t), 91.3 (s), 121.4 (s), 125.1 (d), 127.6 (s), 128.7 (d), 130.7 (d), 132.2 (d), 133.7 (d), 198.4 (s), 203.6 (s), 230.8 (C = W). Anal. Calc. for $C_{18}H_{13}O_6NW$: C, 41.33; H, 2.48; N, 2.67. Found: C, 41.45; H, 2.43; N, 2.61%.

4.9. General procedure for cyclization. Reaction of dicobalt octacarbonyl with complex *3a*

A total of 0.400 g of $Co_2(CO)_8$ (1.2 mmol) were added to 0.570 g of the (allylamino)carbene complex **3a** (1 mmol) in 20 ml of dry THF, and the reaction mixture was left, under Ar, at room temperature (r.t.) for 4 h. The reaction course was monitored by TLC (1:1 hexane–EtOAc). After the starting product had been consumed, the solvent was removed and the residue passed through a flash chromatography column using the mentioned eluent affording two different complexes 0.184 g of **4a** (21% yield) as a dark oil and 0.075 g of **6a** (13% yield) as a red solid.

4a. IR ($CHCl_3$): 3238, 2096, 2032, 1978, 1932 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.34 (s, 3H, CH_3), 4.70 (d, $J = 1$ Hz, 2H, NCH_2), 5.04 (s, 1H, CH_2), 5.49 (s, 1H, CH_2), 7.34–7.42 (m, 5H, Ph), 9.03 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 14.6 (q), 60.2 (t), 104.8 (s), 110.8 (t), 128.6 (d), 128.7 (s), 129.0 (d), 129.5 (d), 137.1 (s), 140.3 (s), 197–198 (bs), 198.2 (s), 201.4 (s), 244.9 (C = W). Anal. Calc. for $C_{24}H_{13}O_{11}NSCo_2W$: C, 34.91; H, 1.57; N, 1.69; S, 3.88. Found: C, 34.70; H, 1.76; N, 1.70; S, 3.87%.

6a. IR ($CHCl_3$): 3400, 2063, 1978, 1915 1718 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.08 (s, 3H, CH_3), 2.97 (d, $J =$

18.3 Hz, 2H, CH_2), 3.09 (d, $J = 18.3$ Hz, 1H, CH_2), 3.83 (d, $J = 12.6$ Hz, 1H, NCH_2), 3.91 (dd, $J = 12.6$, 1.6 Hz, 1H, NCH_2), 7.24–7.50 (m, 5H, Ph), 9.20 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 12.8 (q), 47.8 (t), 55.9 (s), 65.0 (t), 128.4 (d), 128.8 (s), 129.7 (d), 130.3 (d), 137.1 (s), 143.7 (s), 175.4 (s), 197.0 (s), 201.8 (s), 205.2 (s), 239.6 (C = W). Anal. Calc. for $C_{18}H_{13}O_5NSW$: C, 40.21; H, 2.29; N, 2.47; S, 5.64. Found: C, 40.25; H, 2.33; N, 2.38; S, 5.49%.

4.10. Reaction of dicobalt octacarbonyl with complex *3b*

After the reaction of 0.135 g of $Co_2(CO)_8$ (0.4 mmol) and 0.220 g of the (allylamino)carbene complex **3b** (0.35 mmol) under standard conditions, two new complexes separated by flash chromatography (1:1 hexane–ethyl acetate) were obtained from the reaction crude: complex **6b** as an orange–red solid (0.060 g, 26% yield) and **5b** as a red oil (0.015 g, 5% yield).

5b. IR ($CHCl_3$): 2958, 2063, 2044, 2030, 2002, 1940, 1919, cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.78 (d, $J = 15.9$ Hz, 1H, CH_2), 3.33 (d, $J = 14.1$ Hz, 1H, SCH_2), 3.65 (d, $J = 12.9$ Hz, 1H, NCH_2), 3.73 (d, $J = 12.9$ Hz, 1H, NCH_2), 4.22 (dd, $J = 15.9$, 5.1 Hz, 1H, CH_2), 7.30–7.58 (m, 5H, Ph), 8.52 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 43.2 (t), 47.6 (t), 58.4 (s), 67.7 (t), 114.1 (s), 127.6 (d), 128.0 (s), 128.5 (d), 129.0 (d), 129.2 (d), 133.1 (d), 136.5 (s), 197–199 (bs), 198.3 (s), 201.5 (s), 244.3 (C = W).

6b. IR ($CHCl_3$): 3338, 2061, 1984, 1971, 1930, 1895, 1718 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.91 (d, $J = 18.4$ Hz, 1H, CH_2), 3.08 (d, $J = 18.4$ Hz, 1H, CH_2), 3.86 (m, 4H, SCH_2, NCH_2), 7.25–7.47 (m, 5H, Ph), 9.05 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 35.6 (t), 48.1 (t), 57.4 (s), 65.2 (t), 127.8 (d), 128.1 (s), 128.4 (d), 128.9 (d), 129.0 (d), 129.7 (d), 130.3 (d), 135.6 (s), 143.9 (s), 175.5 (s), 197.1 (s), 201.7 (s), 204.5 (s), 240.0 (C = W). Anal. Calc. for $C_{24}H_{17}O_5NSW$: C, 46.65; H, 2.64; N, 2.17; S, 4.97. Found: C, 46.52; H, 2.86; N, 2.07; S, 4.66%.

4.11. Reaction of dicobalt octacarbonyl with complex *3c*

After the reaction of 0.510 g of $Co_2(CO)_8$ (1.5 mmol) and 0.482 g of the (allylamino)carbene complex **3b** (1 mmol) under standard conditions, two new complexes separated by flash chromatography (1:1 hexane–ethyl acetate) were obtained from the reaction crude. Complex **6c** as an orange–red solid (0.120 g, 24% yield) and **6c** as a red oil (0.155 g, 18% yield).

5c. IR ($CHCl_3$): 3402, 2335, 2059, 2042, 2027, 1976, 1936, 1909, cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.82 (d, $J =$ 15.2 Hz, 1H, CH_2), 3.26 (d, $J = 12.8$ Hz, 1H, SCH_2), 3.32 (d, $J = 12.8$ Hz, 1H, SCH_2), 3.61 (d, $J = 13$ Hz, 1H, NCH_2), 3.70 (d, $J = 13$ Hz, 1H, NCH_2), 4.24 (dd, $J = 15.2$, 5 Hz, 1H, CH_2), 7.30–7.58 (m, 5H, Ph), 8.68 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 43.0 (t), 47.4 (t), 58.3 (s), 67.6 (t), 114.3 (s), 127.6 (d), 128.0 (s), 128.7 (d), 129.1 (d), 129.3 (d), 133.1 (d), 136.7 (s), 197–199 (bs), 217.5 (s), 222.2 (s), 254.5 (C = Cr).

6c. IR ($CHCl_3$): 3288, 2054, 1949, 1932, 1905, 1697 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.92 (d, $J = 18.4$ Hz, 1H, CH_2), 3.08 (d, $J = 18.4$ Hz, 1H, CH_2), 3.70–3.92 (m, 4H, SCH_2, NCH_2), 7.26–7.46 (m, 5H, Ph), 9.12 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 35.4 (t), 48.0 (t), 57.3 (s), 64.8 (t), 127.8 (d), 128.3 (s), 128.5 (d), 128.9 (d), 129.1 (d), 129.6 (d), 130.0 (d), 135.6 (s), 144.3 (s), 173.9 (s), 204.8 (s), 216.3 (s), 222.2 (s), 264.6 (C = Cr). Anal. Calc. for $C_{24}H_{17}O_5NSCr$: C, 58.70; H, 3.32; N, 2.74; S, 6.26. Found: C, 58.54; H, 3.41; N, 2.76; S, 6.22%.

4.12. Reaction of dicobalt octacarbonyl with complex *3f*

After the reaction of 0.272 g of $Co_2(CO)_8$ (0.8 mmol) and 0.500 g of the (allylamino)carbene complex **3f** (0.64 mmol) under standard conditions and purification, complex **5f** [10] was obtained as a red solid (0.156 g, 56% yield).

4.13. Reaction of dicobalt octacarbonyl with complex *3g*

After the reaction of 0.272 g of $Co_2(CO)_8$ (0.8 mmol) and 0.300 g of the (allylamino)carbene complex **3g** (0.64 mmol) under standard conditions, and purification, complex **5f** [9] was obtained as a red solid (0.156 g, 41% yield).

4.14. Reaction of dicobalt octacarbonyl with complex *3h*

After the reaction of 0.096 g of $Co_2(CO)_8$ (0.28 mmol) and 0.093 g of the (allylamino)carbene complex **3h** (0.18 mmol) under standard conditions a new complex was obtained, which after purification by flash chromatography (1:1 hexane–ethyl acetate), proved to be a mixture (3/1) of diastereomers of the complex **6h** (0.050 g, 50% yield).

6h. (major isomer) IR ($CHCl_3$): 3388, 2063, 1976, 1940, 1915, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.04 (td, $J = 6.8$, 4.8 Hz, 1H, C*H*), 3.66 (td, $J = 8.4$, 6.8 Hz, 1H, C*H*), 3.85–3.89 (m, 4H, NCH_2), 7.32–7.44 (m, 5H, Ph), 9.19 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 45.5 (d), 49.9 (d), 55.5 (t), 62.1 (t), 128.3 (d), 129.3 (s), 129.5 (s), 130.2 (d), 143.7 (s), 178.7 (s), 197.2 (s), 201.7 (s), 208.6 (s), 238.8 (C = W). MS (FAB$^+$, Xe, matrix NBA) m/e: 551 ($M^+ + 1$), 523, 467, 219, 154 (100%).

6h. (minor isomer) IR ($CHCl_3$): 3180, 2061, 1982, 1938, 1905, 1741 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.74 (dd, $J = 9.3$, 5.1 Hz, 1H, C*H*), 3.52–3.57 (m, 1H, C*H*), 3.98–4.04 (m, 2H, NCH_2), 4.08–4.13 (m, 2H, CH_2),

7.37–7.44 (m, 5H, Ph), 9.10 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 45.5 (d), 48.1 (d), 54.2 (t), 60.4 (t), 128.3 (d), 129.4 (s), 129.5 (s), 130.1 (d), 143.3 (s), 177.6 (s), 197.1 (s), 201.8 (s), 208.3 (s), 238.3 (C = W).

4.15. Reaction of dicobalt octacarbonyl with complex *3d*

After the reaction of 0.372 g of $Co_2(CO)_8$ (1.1 mmol) and 0.452 g of the (allylamino)carbene complex **3d** (0.84 mmol) under standard conditions and separation of the crude by flash chromatography, two new stereoisomeric carbene complexes were obtained: **7d** (0.215 g, 47% yield) and **8d** (0.077 g, 17% yield).

7d. IR ($CHCl_3$): 3413, 2061, 1967, 1928 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.27 (s, 3H, SCH_3), 4.49 (s, 2H, NCH_2), 6.27 (s, 1H, SC*H*), 7.32–7.44 (m, 5H, Ph), 7.85 (s, 1H, C*H*), 9.12 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 19.4 (q), 61.1 (t), 124.4 (s), 127.6 (d), 128.1 (s), 128.7 (d), 130.2 (d), 135.8 (s), 144.8 (d), 145.4 (s), 198.3 (s), 202.4 (s), 245.7 (C = W). Anal. Calc. for $C_{18}H_{13}O_5NSW$: C, 40.07; H, 2.41; N, 2.59; S, 5.93. Found: C, 40.21; H, 2.49; N, 2.53; S, 5.80%.

8d. IR ($CHCl_3$): 3400, 2059, 1960, 1929 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.19 (s, 3H, SCH_3), 4.34 (s, 2H, NCH_2), 6.63 (s, 1H, SC*H*), 7.35–7.58 (m, 5H, Ph), 7.72 (s, 1H, C*H*), 8.77 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 20.2 (q), 61.5 (t), 122.9 (s), 125.8 (d), 128.1 (d), 128.7 (d), 130.1 (d), 135.2 (s), 143.5 (d), 144.9 (s), 198.7 (s), 201.8 (s), 245.7 (C = W).

4.16. Reaction of dicobalt octacarbonyl with complex *3e*

After the reaction of 0.460 g of $Co_2(CO)_8$ (1.3 mmol) and 0.455 g of the (allylamino)carbene complex **3e** (0.97 mmol) under standard conditions and separation of the crude by flash chromatography, two new stereoisomeric carbene complexes were obtained: **7e** (0.165 g, 33% yield) and **8e** (0.152 g, 30% yield).

7e. IR ($CHCl_3$): 3413, 2054, 1971, 1932 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.24 (s, 3H, SCH_3), 4.50 (s, 2H, NCH_2), 6.21 (s, 1H, SC*H*), 7.30–7.41 (m, 5H, Ph), 7.86 (s, 1H, C*H*), 8.83 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 19.5 (q), 60.8 (t), 125.0 (s), 127.6 (d), 128.3 (d), 128.7 (d), 130.1 (d), 135.9 (s), 143.4 (d), 144.5 (s), 218.2 (s), 222.7 (s), 266.2 (C = Cr). Anal. Calc. for $C_{18}H_{13}O_5NSCr$: C, 53.07; H, 3.19; N, 3.44; S, 7.86. Found: C, 52.44; H, 3.42; N, 3.32; S, 7.60%.

8e. IR ($CHCl_3$): 3411, 2054, 1930 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.15 (s, 3H, SCH_3), 4.53 (s, 2H, NCH_2), 6.53 (s, 1H, SC*H*), 7.33–7.55 (m, 5H, Ph), 7.76 (s, 1H, C*H*), 8.84 (bs, 1H, N*H*). ^{13}C-NMR ($CDCl_3$): δ 17.4 (q), 58.8 (t), 124.6 (s), 126.2 (d), 128.1 (d), 128.8 (d), 130.1 (d), 136.0 (s), 143.1 (d), 145.7 (s), 218.1 (s), 222.6 (s), 265.7 (C = Cr).

Acknowledgements

The authors acknowledge the financial support from DGICYT (PB-97-0407-CO5-05) and Generalitat de Catalunya (Grant 5G395-0439).

References

[1] (a) F. Camps, J.M. Moretó, S. Ricart, J.M. Viñas, Angew. Chem. Int. Ed. Engl. 30 (1991) 1470. (b) L. Jordi, S. Ricart, J.M. Viñas, J.M. Moretó, Organometallics 16 (1997) 2808.
[2] L. Jordi, J.M. Moretó, S. Ricart, J.M. Viñas, M. Mejias, E. Molins, Organometallics 11 (1992) 3507.
[3] M.E. Krafft, C.A. Juliano, J. Org. Chem. 57 (1992) 5106.
[4] (a) S.A. Burns, R.J.P. Corriu, H. Huynh, J.J.E. Moreau, J. Organomet. Chem. 333 (1987) 281. (b) J. Barluenga, F.J. Fañanas, F. Toubelo, M. Yus, J. Chem. Soc. Chem. Commun. (1988) 1135. (c) J. Barluenga, R.M. Canteli, J. Flórez, J. Org. Chem. 59 (1994) 602. (d) J. Barluenga, R.M. Canteli, J. Flórez, J. Org. Chem. 59 (1994) 1586.
[5] R. Sabaté, U. Schick, J.M. Moretó, S. Ricart, Organometallics 15 (1996) 3611.
[6] C.P. Casey, N.W. Vollendorf, K.J. Haller, J. Am. Chem. Soc. 106 (1984) 3754.
[7] (a) I.U. Khand, P.L. Pauson, J. Chem. Soc. Chem. Commun. (1974) 379. (b) I.U. Khand, P.L. Pauson, Heterocycles 11 (1978) 59.
[8] (a) M.E. Krafft, C.A. Juliano, J.L. Scott, C. Wright, M.D. McEachin, J. Am. Chem. Soc. 113 (1991) 1693. (b) M.E. Krafft, A.M. Wilson, O.A. Dasse, L.V.R. Bonaga, Y.Y. Cheung, Z. Fu, B. Shao, I.L. Scott, Tetrahedron Lett. 39 (1998) 5911.
[9] K.H. Dötz, W. Kuhn, J. Organomet. Chem. 286 (1985) C23.
[10] This complex has been described in Ref. [1a].