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Journal of Organometallic Chemistry 691 (2006) 5753–5766
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis of heterocyclic carbene ligands via 1,2,3-diheterocyclization of allenylidene complexes with dinucleophiles

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Received 8 June 2006; received in revised form 18 July 2006; accepted 25 July 2006
Available online 19 September 2006

Dedicated to Professor Bogdan Marciniec on the occasion of his 65th birthday.

Abstract

Heterocyclic carbene complexes are accessible from π-donor-substituted allenylidene complexes, $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)Ph]$ (**1**) and $[(CO)_5Cr{=}C{=}C{=}C(O\text{-}endo\text{-Bornyl})OEt]$ (**4**), and various dinucleophiles by 1,2,3-diheterocyclization. The reaction of **1** with 1,2-dimethylhydrazine gives the 1,2-dimethylpyrazolylidene complex $[(CO)_5Cr{=}C\text{-}C(H){=}C(Ph)\text{-}NMe\text{-}NMe]$ (**2**) in high yield in addition to small amounts of the α,β-unsaturated carbene complex $[(CO)_5Cr{=}C(NMe_2)\text{–}C(H){=}C(NMe_2)Ph]$ (**3**). The analogous reaction of **4** with 1,2-dimethylhydrazine affords the 1,2-dimethylpyrazolylidene complex $[(CO)_5Cr{=}C\text{-}C(H){=}C(O\text{-}endo\text{-Bornyl})\text{-}NMe\text{-}NMe]$ (**5**) and, via displacement of the C_γ-bound ethoxy substituent, the hydrazinoallenylidene complex $[(CO)_5Cr{=}C{=}C{=}C(O\text{-}endo\text{-Bornyl})\{NMe\text{-}N(H)Me\}]$ (**6**). Treatment of **6** with catalytic amounts of acids induces cyclization to **5**. On addition of 1,1-dimethylhydrazine to **1** the zwitterionic pyrazolium-5-ylidene complex $[(CO)_5Cr\text{-}C{=}C(H)\text{-}C(Ph){=}N\text{-}NMe_2]$ (**7**) is formed. The reaction of **1** with 1,2-diaminocyclohexane affords a octahydro-benzo[1,4]diazepinylidene complex (**10**) and, via intermolecular substitution, a binuclear bisallenylidene complex (**11**). Thiazepinylidene complexes (**12**–**14**), containing 7-membered N/S-heterocyclic carbene ligands, are formed highly selectively in the reaction of **1** with 2-aminoethanethiol or related cysteine derivatives by a substitution/cyclization sequence. The analogous reaction of **1** with homocysteine methylester yields a thiazocanylidene complex (**15**). All new heterocyclic carbene ligands are strong donors exhibiting σ-donor/π-acceptor ratios similar to those of the known imidazolylidene complexes. On photolysis of **2** and **12** in the presence of triphenylphosphine, the corresponding *cis*-carbene tetracarbonyl triphenylphosphine complexes (**16** and **17**) are formed. The solid state structure of complexes **2**, **7**, **14**, **15**, and **16** is established by X-ray structural analysis.

Keywords: Allenylidene complexes; Chromium; Pyrazolylidene complexes; Cyclization; Heterocyclic carbene ligands

1. Introduction

The first planned synthesis of transition metal carbene complexes was reported by Fischer and Maasböl in 1964 [1]. Since then, a series of syntheses has been developed [2]. A large number of experimental and theoretical studies gives insight into the structures and properties of this versatile class of organometallic compounds that has evolved into a very powerful tool in organic and organometallic synthesis [3]. The first complexes containing N-heterocyclic ligands (imidazolylidene ligands) were described in 1968 by Öfele (chromium complexes) [4] and Wanzlick (mercury complexes) [5]. The first complexes containing C–C saturated N-heterocyclic ligands (imidazolinylidene

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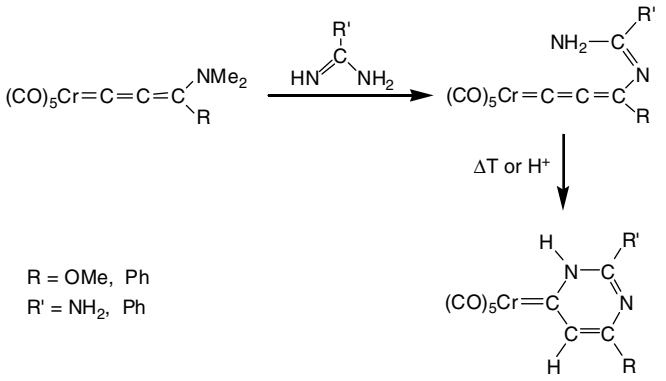
doi:10.1016/j.jorganchem.2006.07.049

ligands) were reported by Lappert several years later in 1972 [6]. Subsequently, imidazolinylidene complexes of many transition metals have been prepared [7]. Since the isolation of the first free N-heterocyclic carbenes by Arduengo et al. [8] and the elaboration of versatile synthetic procedures, numerous imidazolylidene complexes have been synthesized [9]. Only recently was it recognized that N-heterocyclic carbenes (NHCs) can act as very powerful co-ligands in homogeneous catalysts and can replace phosphine ligands in these complexes [10]. Thus NHC complexes play an increasingly important role in homogeneous catalysis. Until now, most studies on the catalytic activity of NHC complexes deal with imidazolylidene complexes. Therefore, attention has been extended to other heterocyclic ligand systems exploring their potential [11].

Usually, NHC complexes are synthesized from free carbenes (or their precursors, imidazolium salts) and suitable transition metal complexes. An alternative approach would involve cycloaddition of a dinucleophile to the allenylidene ligand in $[L_nM{=}C_\alpha{=}C_\beta{=}C_\gamma(R^1)R^2]$ complexes [12]. The linear unsaturated allenylidene ligand consists of an alternating array of electrophilic and nucleophilic centers, C_α and C_γ exhibiting electrophilic character. We were able to show that neutral dihydropyrazolylidene and dihydrooxazolylidene complexes of chromium and tungsten are accessible by reaction of hydrazines and hydroxylamines with bis(aryl)allenylidene complexes [13]. The first step in these reactions involves addition of the nucleophile across the C_α–C_β bond of the allenylidene ligand followed by acid-catalyzed cyclization. Five- and six-membered heterocyclic ligands were also obtained by Esteruelas et al. by reaction of cationic ruthenium allenylidene complexes with various dinucleophiles such as pyrazole, 2-aminopyridine or thioisonicotinamide [14]. The reaction of the rhenium cation $[(triphos)(CO)_2Re{=}C{=}C{=}CPh_2]^+$ with 1*H*-benzotriazole, 2-aminopyridine or 2-aminothiazole likewise afforded 5- and 6-membered heterocyclic ligands [15]. All of these reactions proceed by the addition-cyclization scheme.

We recently reported that the reactions of π-donor-substituted allenylidene pentacarbonyl complexes with dinucleophiles deviate from those observed for bis(aryl)allenylidene pentacarbonyl complexes. The reaction of $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)R]$ (R=Ph, OMe) with for example amidines, guanidine and thioacetamide affords likewise diheterocyclization products. However, the formation of the resulting complexes is initiated by substitution of the dinucleophiles for one of the C_γ-substituents. The subsequent cyclization by addition of the N–H functionality across the C_α–C_β bond (thermally induced or H^+-catalyzed) then yields the corresponding unsaturated 6-membered heterocyclic ligand (e.g. Scheme 1) [16]. We now report that this reaction scheme is also applicable to the synthesis of pyrazolylidene ligands as well as to the synthesis of 7- and 8-membered heterocyclic carbene ligands.



Scheme 1.

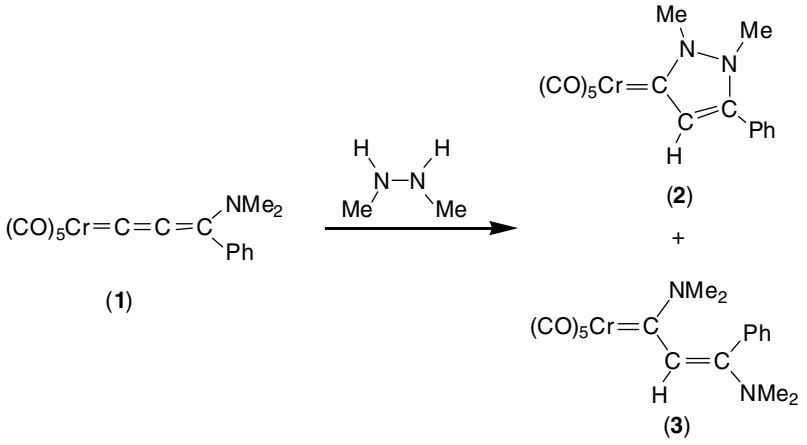
2. Results and discussion

2.1. Diheterocyclization of allenylidene complexes

Treatment of a solution of complex **1** in tetrahydrofuran with 1.1 equivalents of an aqueous solution of 1,2-dimethylhydrazine and gentle warming for 120 min gave, after chromatographic workup, a mixture of the pyrazolylidene complex **2** and the alkenyl(amino)carbene complex **3** in 91% and 4% yield, respectively (Scheme 2). Both complexes had previously been prepared by alternative methods. Complexes **2** and **3** were identified by comparison of their spectroscopic data with those published [17].

The formation of pyrazolylidene complex **2** is readily explained by initial substitution of dimethylhydrazine for the terminal dimethylamino substituent of **1** to form a hydrazinoallenylidene complex. Such a substitution reaction is in accord with the known reactivity pattern of donor-substituted allenylidene complexes [16,18]. Similar substitution reactions are used to replace alkoxy substituents in electrophilic alkoxycarbene complexes (Fischer-type carbene complexes) by other π-donor groups [19] and have been studied in detail by kinetic means [20]. The substitution is followed by addition of the "second" N–H functionality across the C_α–C_β bond of the allenylidene ligand. It was neither possible to isolate nor spectroscopically detect the hydrazinoallenylidene complex intermediate. Therefore, the cyclization step must be fast compared to the initial substitution reaction. The alternative sequence – addition of the hydrazine across the C_α–C_β bond of the allenylidene ligand as initiating step followed by substitution/cyclization – can be excluded. The initial addition product thus formed (a hydrazinocarbene complex) is expected to be stable. Several hydrazinocarbene complexes have been isolated [13,21] and structurally characterized [21a–c].

The alkenyl(amino)carbene complex **3** presumably is formed by addition of dimethylamine across the C_α–C_β bond of the allenylidene ligand of **1**. Dimethylamine is a co-product in the first substitution step (see above). Surprisingly, no reaction was observed when allenylidene complex **1** was replaced by the ethyl(methyl)aminoallenylidene complex **8** having N(Et)Me instead of NMe_2 as



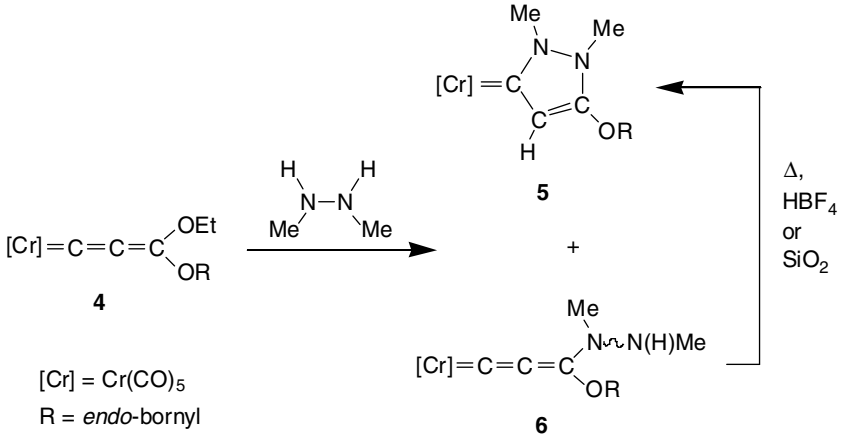
Scheme 2.

one of the substituents at C_γ. Increasing the temperature or extending the reaction times only led to slow decomposition of the starting complex. Obviously, the reactivity of such allenylidene complexes strongly depends on the steric requirements of the terminal substituents.

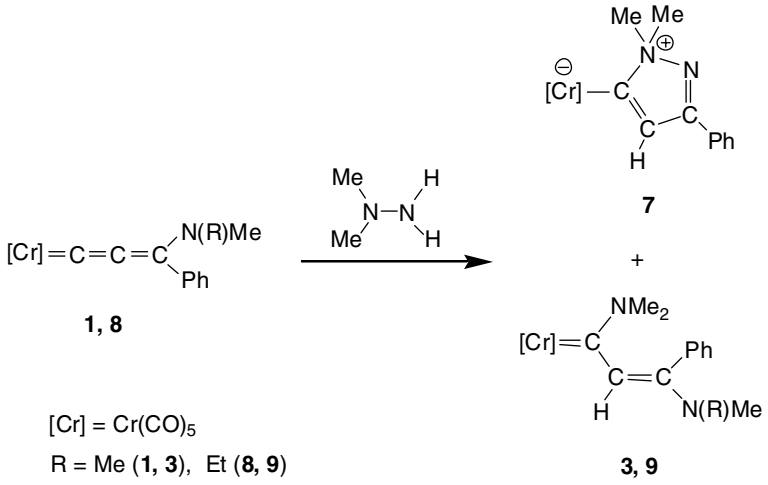
The mechanistic proposal is supported by the results of the reaction of bis(alkoxy)allenylidene complex **4** with 1,2-dimethylhydrazine. Treatment of **4** with 1,2-dimethylhydrazine afforded a mixture of the pyrazolylidene complex **5** and the hydrazinoallenylidene complex **6** (61% and 35% yield, respectively). The reaction is highly selective. Only products derived from displacement of the ethoxy group were observed. The hydrazinoallenylidene complex **6** is stable in solution at ambient temperature for several hours. However, when heating solutions to 50 °C compound **6** readily transformed into the pyrazolylidene complex **5**. Addition of catalytic amounts of HBF_4 or silica likewise induced the cyclization (Scheme 3). These observations confirm that the 1,2,3-diheterocyclization proceeds by a stepwise process and is initiated by addition of the dinucleophile to the C_γ atom of the allenylidene ligand and displacement of one of the two C_γ substituents.

When 1.1 equivalents of 1,1-dimethylhydrazine instead of 1,2-dimethylhydrazine were added to complex **1** and the solutions were heated to 50 °C, a mixture of the pyrazolium complex **7** (75%) and again the alkenyl(amino)carbene complex **3** (21%) were obtained (Scheme 4). As already observed with 1,2-dimethylhydrazine, the related ethyl(methyl)aminoallenylidene complex **8** is also less reactive towards 1,1-dimethylhydrazine. When the same reaction conditions were employed, the complete conversion of **8** required an approximately fivefold extension of the reaction times. Again the pyrazolium complex **7** was formed albeit, in only poor yield (19%). The major product (68%) was the alkenyl(amino)carbene complex **9** related to **3** (Scheme 4).

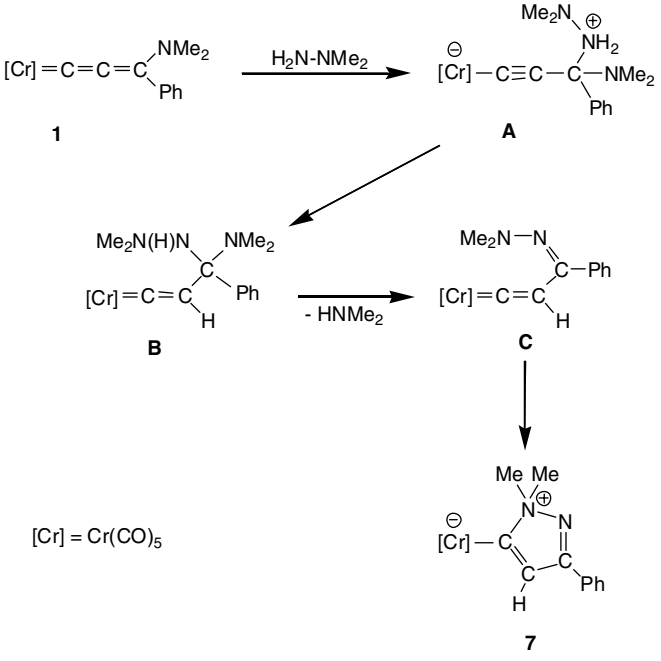
A likely mechanism for the formation of **7** is depicted in Scheme 5. The first reaction step involves nucleophilic attack of the unsubstituted nitrogen atom of the hydrazine at the terminal carbon atom of the allenylidene ligand. Subsequent 1,2-hydrogen shift in the resulting alkynyl complex intermediate **A** affords the vinylidene complex **B**. Elimination of dimethylamine and rearrangement leads to the formation of vinylidene complex **C**. A similar reaction



Scheme 3.



Scheme 4.



Scheme 5.

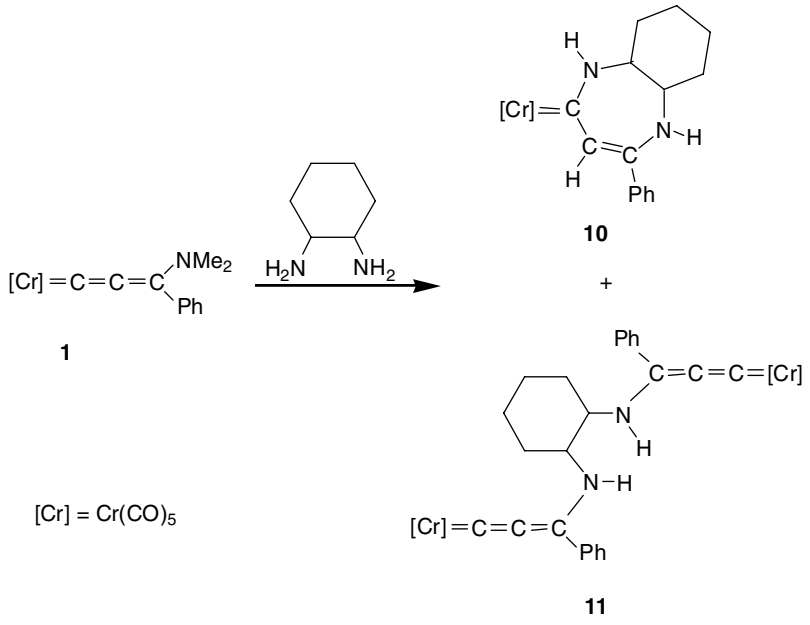
path has already been proposed for the reaction of amino-allenylidene complexes with amines [18] or acetylides [22]. Nucleophilic addition of the dimethylamino-substituted nitrogen atom to the electrophilic α-carbon atom of the vinylidene species finally completes the reaction sequence. Complex **9** is formed, analogously to complex **3**, by addition of dimethylamine across the C_α–C_β bond of the allenylidene ligand of the starting allenylidene complex.

It is noteworthy that compared to the reaction of bis(aryl)allenylidene complexes with hydrazines those of **1** or **8** require elevated temperatures and extended reaction times. This emphasizes once more the importance of the donor-substituents at the terminal carbon atom for the stabilization of the complexes. The effect is even more pronounced for allenylidene complexes with sterically demanding amino substituents at the terminal carbon atom (even when the changes are of only minor degree). Consequently, the amino-substituted allenylidene complexes **1** and **8** do not react any more with less basic or sterically more hindered hydrazines like for example diphenylhydrazine, diethylhydrazine, and di-*iso*-propylhydrazine. The reduced reactivity cannot be compensated by prolonged reaction times since decomposition of the starting material strongly competes with the reaction with hydrazines. When diphenylhydrazine was employed the major isolated product was $[Cr(CO)_6]$. A displacement of the allenylidene ligand by the N-nucleophile was observed in the reaction of allenylidene complex **1** with *N*-methylhydroxylamine or pyrazole [23].

The related reaction of π-donor-substituted allenylidene complexes with 1,3-dinucleophiles leads, as previously described, to the formation of 6-membered heterocyclic carbene complexes containing pyrimidinylidene, thiazylidene and pyrazolopyrimidinylidene ligands [16]. In all of these reactions the favored reaction pathway is an initial addition of the nucleophile to the C_γ atom of the cumulenylidene ligand followed by intramolecular cyclization. In none of the reactions investigated so far products derived from an intermolecular coupling with a second allenylidene complex could be detected.

In contrast, when a solution of **1** is treated with a 20-fold excess of 1,2-diaminocyclohexane (as an example for a ''rigid'' 1,4-dinucleophile) in addition to the octahydro-[1,4]benzodiazepinylidene complex **10** (31% chemical yield), containing an unsaturated di-N-heterocyclic 7-membered carbene ligand, the binuclear allenylidene complex **11** was isolated in 28% yield (56% with respect to the $(CO)_5Cr$ fragment) (Scheme 6). Complex **10** is again obtained via substitution and diheterocyclization and complex **11** by intermolecular disubstitution.

Complexes containing unsaturated N,S-heterocyclic 7-membered carbene ligands were obtained in high yield



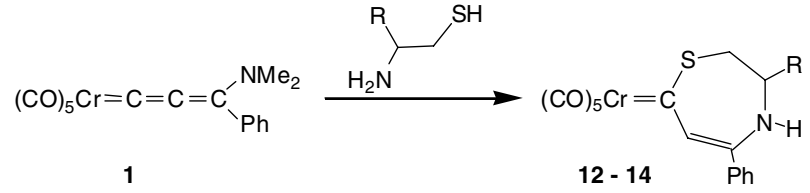
Scheme 6.

from the reaction of **1** with 2-amino-ethanethiol or the related L-cysteine methyl or ethyl ester (both 97% enantiomerically pure) as the dinucleophiles. The thiazepinylidene complexes **12**–**14** were isolated as the only products in 69–87% yield (Scheme 7). The diheterocyclization is highly regioselective. In all product complexes the nitrogen atom is connected to the C_γ atom of the allenylidene ligand and the sulphur atom to C_α.

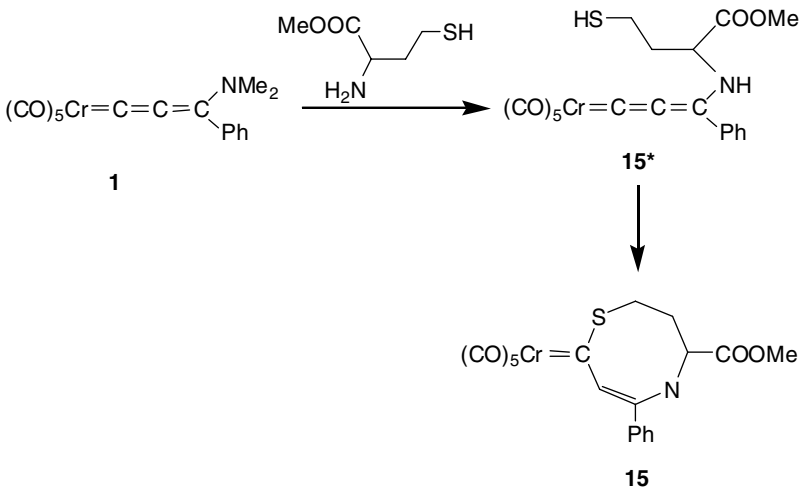
The related reaction of **1** with a racemic mixture of homocysteine methyl ester gave the 8-membered monounsaturated N,S-heterocyclic carbene complex **15**. The thiazocanylidene complex **15** was isolated, after chromatographic workup, in 69% yield (Scheme 8). As with 2-amino-ethanethiol and L-cysteine esters the reaction of **1** with homocysteine methyl ester proceeds highly selectively. Binuclear complexes like for instance **11** were not observed. In contrast to the reactions shown in Scheme 7 the initial substitution product, allenylidene complex **15***, could be detected spectroscopically (ν(CO): 2078 m, 1939 vs, 1915 s; ν(CCC): 1988 m). This once more confirms the mechanistic proposal for the diheterocyclization.

2.2. Reactivity towards triphenylphosphine

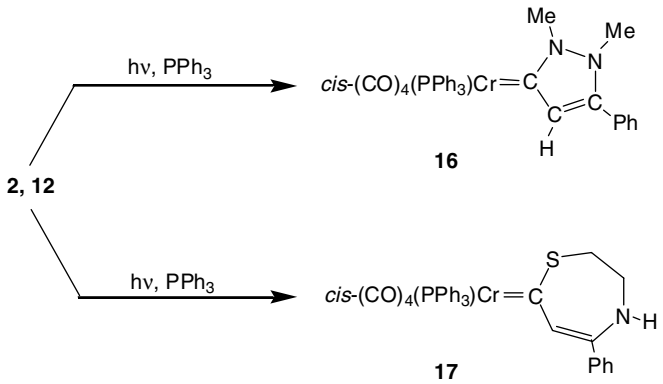
At elevated temperatures alkyl- and aryl(methoxy)carbene complexes react with tertiary phosphines by displacement of one CO ligand to form mixtures of *cis*- and *trans*-carbene(tetracarbonyl)phosphine complexes [24]. When the same reaction conditions were applied to the heterocyclic carbene complexes **2** and **12** no reaction was observed with triphenylphosphine. However, photolysis of **2** and **12** in the presence of triphenylphosphine afforded the *cis*-carbene(tetracarbonyl)triphenylphosphine complexes **16** and **17** in, after chromatography, 87% and 59% yield (Scheme 9). Neither formation of the corresponding *trans* isomer or of isomeric mixtures could be detected nor could an *cis*/*trans* isomerization be induced by heating solutions of **16** and **17** in toluene for 5 h up to 80 °C. In contrast, *cis*- as well as *trans*-alkylcarbene(tetracarbonyl)triphenylphosphine complexes of chromium and tungsten isomerize in solution at 60 °C already within about 20 min to form equilibrium mixtures of the corresponding *cis* and *trans* isomers [25].



Scheme 7.



Scheme 8.



Scheme 9.

2.3. Spectroscopic and structural results

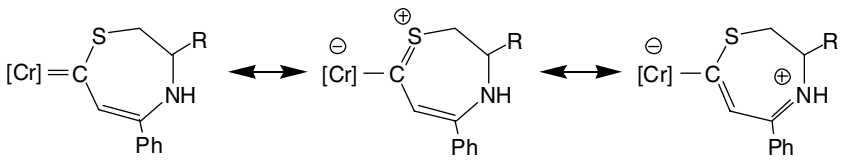
All new complexes were characterized by spectroscopic means and elemental analyses. From the IR spectra it follows that all heterocyclic ligands are strong donors. Surprisingly, the donor properties of the 7- and 8-membered thiacycles in **12**–**15** are only slightly less pronounced than those of the 5-membered pyrazolylidene ligands in **2** and **5**. Those of the 7-membered octahydro-[1,4]diazepinylidene in **10** and of the 5-membered pyrazolylidene ligands in **5** are even identical. There is only a small difference in the donor properties of the two 7-membered heterocyclic ligands in **10** and **12** containing a C_α-bound sulphur atom (**10**) or nitrogen atom, respectively. Due to the much weaker π-donor ability of sulphur a pronounced difference would have been expected comparable to that observed with non-cyclic alkenyl(alkylthio)- and alkenyl(alkylamino)carbene complexes [26]. From these observations a considerable contribution of the resonance form **III** (Scheme 10) to the overall bonding can be deduced.

The allenylidene complexes **6** and **11** exhibit all characteristic features of π-donor-substituted allenylidene complexes. The *ν*(CCC)-absorption in the IR-spectrum of **6** and of related N/O-substituted allenylidene complexes such as $(CO)_5Cr{=}C{=}C{=}C(NMe_2)OMe$ [17b] or $(CO)_5Cr{=}C{=}C{=}C(NMe_2)OMenthyl$ [27] is found at a similar wavenumber. Due to the strong donor character of the terminal substituents the resonance of the metal bound α-carbon atom in the ^{13}C NMR spectrum is found at rather low field. Such allenylidene complexes are better described as iminium-alkinyl zwitterions. The strong delocalisation of the lone pair at the nitrogen atom towards the metal center (Scheme 11) results in a partial double bond of the C_γ–N-bond which becomes manifest in two sets of signals for the N-bound groups (*E*- and *Z*-isomers) as well as for the atoms of the allenylidene carbon chain and even for the *trans*-carbonyl carbon atom.

The resonance of the carbene carbon atom in the ^{13}C NMR spectra strongly depends on the type and the size of the ring system. As expected, the C_α resonance of the pyrazolylidene complexes **2** and **5** is found at rather high field ($\delta = 187.4$ and 189.9 ppm, respectively), that of the sulphur-containing heterocyclic complexes **12**–**15** at significantly lower field ($\delta = 271$–278 ppm). The C_α resonance of the octahydro-benzo[1,4]diazepinylidene complex in **10** and of **7** is observed at an intermediate position ($\delta = 249.2$ and 234.4 ppm, respectively).

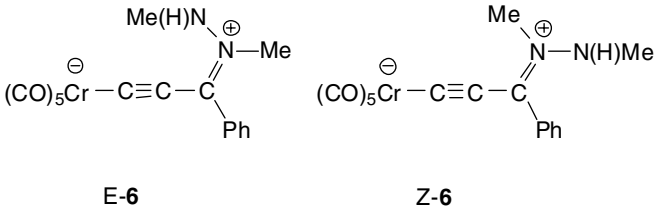
The introduction of the phosphine donor causes only a slight change in the ^{13}C-resonances of the heterocyclic ring system. The C_α-resonance of **16** is slightly shifted downfield (from 187 ppm to 197 ppm) whereas the carbene resonance of **17** is shifted upfield (from 270 ppm to 257 ppm) with respect to the corresponding pentacarbonyl complexes **2** and **12**. The effect on the other carbon nuclei is negligible.

The solid-state structures of the complexes **2** (Fig. 1), **7** (Fig. 2), **14** (Fig. 3), **15** (Fig. 4),and **16** (Fig. 5) were additionally established by X-ray analyses. Unfortunately, the crystals of **2** were of rather poor quality and contained half a strongly disordered molecule of dichloromethane per unit cell. However, the distances and angles of **2** agree very well



I II III

Scheme 10.



E-6 Z-6

Scheme 11.

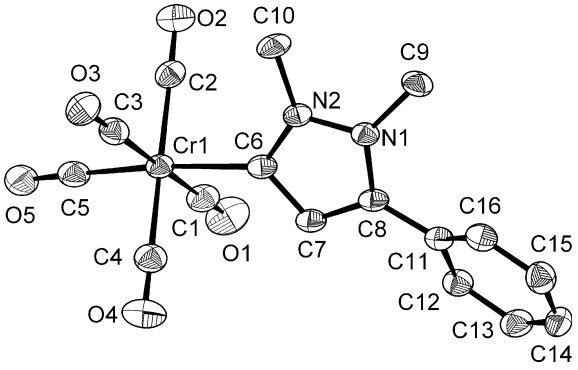
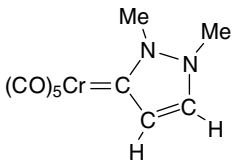


Fig. 1. Structure of complex **2**, half a molecule of CH_2Cl_2 in the unit cell is omitted (ellipsoids drawn at 50% level, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Cr(1)–C(1) 1.910(4), Cr(1)–C(2) 1.897(4), Cr(1)–C(3) 1.908(4), Cr(1)–C(4) 1.916(4), Cr(1)–C(5) 1.870(4), Cr(1)–C(6) 2.144(4), C(6)–C(7) 1.415(5), C(7)–C(8) 1.380(5), C(8)–N(1) 1.365(4), N(1)–N(2) 1.387(4), N(2)–C(6) 1.358(4); Cr(1)–C(6)–C(7) 126.4(2), C(6)–C(7)–C(8) 110.3(3), C(7)–C(8)–N(1) 107.1(3), C(8)–N(1)–N(2) 107.2(3), N(1)–N(2)–C(6) 111.7(3), N(2)–C(6)–Cr(1) 129.7(3).

with those found for the unsubstituted *N*,*N*′-dimethylpyrazolylidene complex **18** [28].



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The pyrazolylidene ring in **2** (Fig. 1) and in the phosphine-substituted complex **16** (Fig. 5) is essentially planar and the plane of the ring bisects the *cis*-CO ligands. Within error limits the distances within the ring in **2** and **16** are identical.

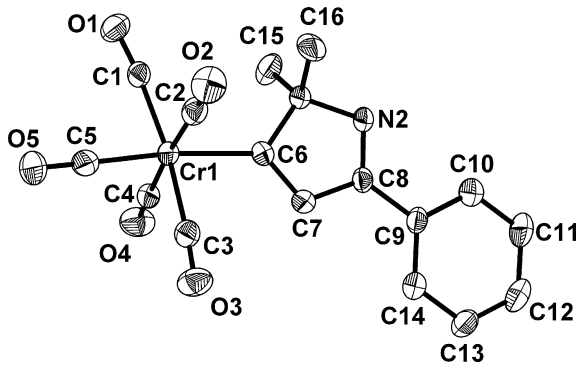


Fig. 2. Structure of complex **7** (ellipsoids drawn at 50% level, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Cr(1)–C(1) 1.893(3), Cr(1)–C(2) 1.903(3), Cr(1)–C(3) 1.916(3), Cr(1)–C(4) 1.910(3), Cr(1)–C(5) 1.862(3), Cr(1)–C(6) 2.132(2), C(6)–C(7) 1.344(3), C(7)–C(8) 1.456(3), C(8)–N(2) 1.370(4), N(1)–N(2) 1.485(3), N(1)–C(6) 1.525(3); Cr(1)–C(6)–C(7) 130.3(2), C(6)–C(7)–C(8) 111.5(2), C(7)–C(8)–N(2) 113.0(2), C(8)–N(2)–N(1) 104.3(2), N(2)–N(1)–C(6) 109.3(2), N(1)–C(6)–Cr(1) 127.8(2).

The tilt of the phenyl plane against the pyrazolylidene plane (torsion angle N(1)–C(8)–C(11)–C(16) = 41.8° in **2** and 47.9° for the analogous angle in **16**) excludes significant

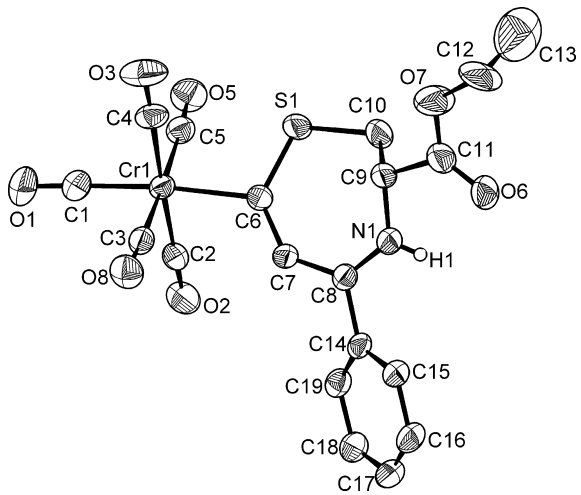


Fig. 3. Structure of complex **14** (ellipsoids drawn at 50% level, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Cr(1)–C(1) 1.861(4), Cr(1)–C(2) 1.914(4), Cr(1)–C(3) 1.898(4), Cr(1)–C(4) 1.894(4), Cr(1)–C(5) 1.906(4), Cr(1)–C(6) 2.149(4), C(6)–C(7) 1.400(5), C(7)–C(8) 1.409(5), C(8)–N(1) 1.324(5), N(1)–C(9) 1.441(5), C(9)–C(10) 1.544(5), C(10)–S(1) 1.820(4), S(1)–C(6) 1.704(4); Cr(1)–C(6)–C(7) 122.0(3), C(6)–C(7)–C(8) 135.0(4), C(7)–C(8)–N(1) 125.7(4), C(8)–N(1)–C(9) 126.3(3), N(1)–C(9)–C(10) 111.3(4), C(9)–C(10)–S(1) 110.0(3), C(10)–S(1)–C(6) 110.6(2), S(1)–C(6)–Cr(1) 109.8(2).

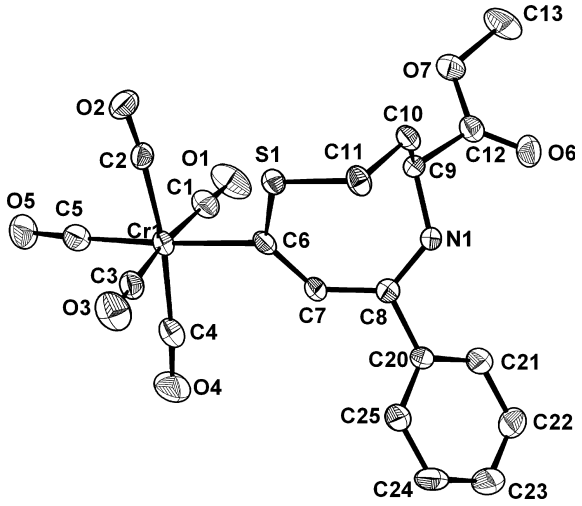


Fig. 4. Structure of complex **15** (ellipsoids drawn at 50% level, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Cr(1)–C(1) 1.910(4), Cr(1)–C(2) 1.893(4), Cr(1)–C(3) 1.905(3), Cr(1)–C(4) 1.904(4), Cr(1)–C(5) 1.867(4), Cr(1)–C(6) 2.129(3), C(6)–C(7) 1.411(5), C(7)–C(8) 1.412(5), C(8)–N(1) 1.329(5), N(1)–C(9) 1.453(5), C(9)–C(10) 1.534(5), C(10)–C(11) 1.520(5), C(11)–S(1) 1.820(4), S(1)–C(6) 1.709(4); Cr(1)–C(6)–C(7) 122.5(3), C(6)–C(7)–C(8) 135.6(3), C(7)–C(8)–N(1) 128.0(3), C(8)–N(1)–C(9) 127.3(3), N(1)–C(9)–C(10) 111.0(2), C(9)–C(10)–C(11) 110.7(3), C(10)–C(11)–S(1) 111.7(3), C(11)–S(1)–C(6) 112.4(2), S(1)–C(6)–Cr(1) 110.9(2).

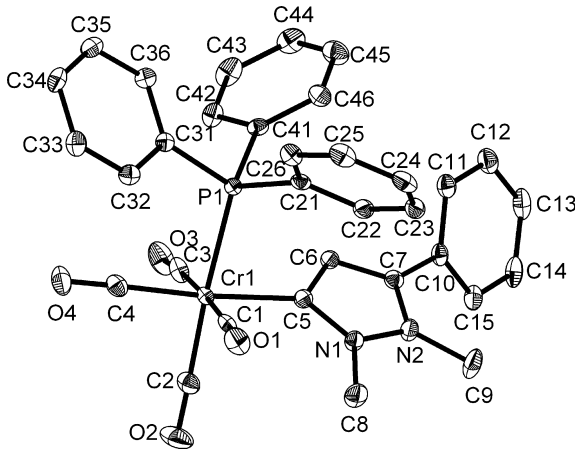


Fig. 5. Structure of complex **16** (ellipsoids drawn at 50% level, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Cr(1)–C(1) 1.883(3), Cr(1)–C(2) 1.848(3), Cr(1)–C(3) 1.902(2), Cr(1)–C(4) 1.858(3), Cr(1)–C(5) 2.126(2), C(5)–C(6) 1.416(3), C(6)–C(7) 1.378(3), C(7)–N(2) 1.354(3), N(1)–N(2) 1.386(3), N(1)–C(5) 1.359(3), Cr(1)–P(1) 2.3910(8); Cr(1)–C(5)–C(6) 127.9(2), C(5)–C(6)–C(7) 110.3(2), C(6)–C(7)–N(2) 107.4(2), C(7)–N(2)–N(1) 107.3(2), N(2)–N(1)–C(5) 111.8(2), N(1)–C(5)–Cr(1) 128.7(2).

interaction between both π-system. The conclusion is supported by identical distances for C(7)=C(8) in **2**, **16**, and **18**. Replacing one *cis*-CO ligand in **2** by triphenylphosphine (**2** → **16**) results in an only slight reduction of the Cr–carbene bond length indicating that Cr–carbene back-donation is of minor importance in stabilizing the complex. This is in accord with an only small effect on the orientation of the pyrazolylidene plane with respect to the *cis*-CO ligands. In **2** the torsion angle C(3)–Cr–C(6)–N(2) is 52.3° (57.5° in **18** [28]). The corresponding angle in **16** is 57.5°. In case of a pronounced back-donation a torsion angle P–Cr–C–N of close to 90° would be expected. Both *trans*-Cr–CO bonds in **16** are significantly shorter than the Cr–CO bonds *cis* to the PPh_3 and the pyrazolylidene ligand and are almost equal in length indicating that both ligands exhibit pronounced but similar donor propensities.

Shifting the methyl substituent from the remote nitrogen atom to the one adjacent to the carbene carbon atom (**2** → **7**) gives rise to a strong change of the distances within the ring. Changing the hybridization of the C6-bound nitrogen from sp^2 to sp^3 prevents π-interaction of N1 with C6. Consequently this bond elongates and corresponds to a C–N single bond in **7** (Fig. 2). The remaining distances within the ring are likewise strongly affected. The bonds C6–C7 and C8–N decrease to values characteristic for C–C and C–N double bonds. Conversely, C7–C8 elongates from 1.380(5) Å to 1.456(3) Å characteristic for $C(sp^2)$–$C(sp^2)$ single bonds. The ring is planar and the plane almost coincides with the plane formed by the atoms Cr, C1, C3, and C5 (torsional angle C1–Cr–C6–N1: 15.9(2)°). The resonance structure of **7** suggests considerable electron transfer from the heterocyclic ligand to the pentacarbonyl fragment and consequently strong Cr–CO back-bonding. However, the assumption is neither corroborated by the Cr–CO distances nor by the *ν*(CO) vibrations. From the *ν*(CO) vibrations even a small decrease in the donor properties can be deduced.

The agreement of the Cr–CO distances in **14** and **15** with those in **5** and **18** [17] is in accordance with the similarity in the donor properties of the 5-, 7- and 8-membered carbene ligands in **2**, **5**, **10**, **12**–**14**, and **15** as deduced from the IR spectra. The Cr(1)–C(6) bond in both complexes is rather long (2.149(4) Å in **14** and 2.129(3) Å in **15**) when compared with Fischer-type thiocarbene complexes (e.g. 2.020(3) Å in $[(CO)_5Cr{=}C(SPh)Me]$ [29]), however, corresponds to that in **5** (2.144(4) Å) and **18** (2.1327(4) Å). The long Cr(1)–C(6) bond and the short C(8)–N(1) bond (1.324(5) Å in **14** and 1.329(5) Å in **15**) confirm the relative importance of the zwitterionic resonance structure **III** (Scheme 10) for the overall bond description. The thiazepinylidene ligand in **14** and the thiazocanylidene ligand in **15** adopt a semi-chair conformation. The fragments C(10), S(1), C(6), C(7), C(8) in **14** and C(11), S(1), C(6), C(7), C(8) in **15** deviate only slightly from planarity (torsion angles: S(1)–C(6)–C(7)–C(8) 5.9° (**14**) and 1.1° (**15**), C(10)–S(1)–C(6)–C(7) −4.4° (**14**), C(11)–S(1)–C(6)–C(7) −1.2° (15)) and are staggered with respect to the *cis*-CO ligands (torsion angle C(4)–Cr(1)–C(6)–S(1) = 49.32(2)° for 14 and C(2)–Cr(1)–C(6)–S(1) = 16.04°(2)).

In summary, 1,2,3-diheterocyclization of dinucleophiles with π-donor-substituted allenylidene complexes offers an easy access to complexes with heterocyclic carbene ligands of various ring sizes and steric requirements. All of these carbene ligands are characterized by strong donor properties and surprisingly similar σ-donor/π-acceptor ratios.

3. Experimental

3.1. General

All operations were performed in an inert gas atmosphere using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), $LiAlH_4$ (pentane) and sodium (THF). The silica gel used for chromatography (Baker, silica for flash chromatography) was argon-saturated. The yields refer to analytically pure substances and are not optimized. Instrumentation: ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded with Jeol JNX 400 and Varian Inova 400 spectrometer at ambient temperature. Chemical shifts are relative to the residual solvent (^1H, ^{13}C) or to 100% H_3PO_4 (^{31}P). IR: Biorad FTS 60. UV–Vis: Hewlett–Packard diode array spectrophotometer 8453. MS: Finnigan MAT 312. Elemental analyis: Heraeus CHN-O-Rapid. The following compounds were prepared according to the literature procedures: **1**, **8** [17b], **4** [27], 2-Amino-4-mercapto-butyric acid methylester [30]. All other chemicals were used as obtained from commercial suppliers.

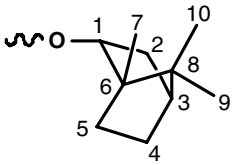
3.2. Pentacarbonyl(1,2-dimethyl-5-phenylpyrazol-3-ylidene)chromium (2) and pentacarbonyl{1,3-bis(dimethylamino)-3-phenylprop-2-en-1-ylidene}chromium (3)

At room temperature a solution of 1.1 mmol of 1,2-dimethylhydrazine in 3 ml of degassed water (prepared in situ by adding an equimolar amount of a concentrated NaOH-solution to 146 mg of 1,2-dimethylhydrazine dihydrochloride) was added to a solution of 0.35 g (1 mmol) of **1** in 5 ml of THF. The reaction mixture was warmed to 50 °C and the progress of the reaction was monitored by IR spectroscopy. When all of the starting material was consumed, the solvent was removed in vacuo and the oily residue purified by chromatography on silica gel at −20 °C using mixtures of pentane/CH_2Cl_2 (increasing polarity from 2:1 to 1:2) as eluent. The first yellow fraction contained the alkenylcarbene complex **3** (16 mg; 0.04 mmol; 4%). The second pale yellow fraction was collected and the solvent removed in vacuo yielding 0.33 g (0.91 mmol; 91%) of pyrazolylidene complex **2**. The complexes **2** and **3** were identified by comparison of their spectroscopic data with those published in the literature [17].

3.3. Pentacarbonyl(1,2-dimethyl-3-endo-bornyloxypyrazol-5-ylidene)chromium (5) and pentacarbonyl(3-N,N′-dimethylhydrazine-3-endo-bornyloxy-1,2-propadienylidene)-chromium (6)

The synthesis of complexes **5** and **6** from 146 mg of 1,2-dimethylhydrazine dihydrochloride and 0.43 g (1 mmol) of **4** in 5 ml of THF at room temperature (reaction time 30 min.) and the chromatography with pentane/CH_2Cl_2 (increasing polarity from 4:1 to 1:1) were carried out analogously to 3.2. The first colourless fraction contained the pyrazolylidene complex **5** (colourless oil; 0.20 g; 0.45 mmol; 45%), the second yellow one complex **6**. After removal of the solvent complex **6** was obtained (yellow oil; 0.19 g, 0.42 mmol; 42%) as a 1:1 mixture of inseparable *E*- and *Z*-isomers (as calculated from the integrals of the ^1H-resonances).

The carbon and hydrogen atoms of the *endo*-bornyl substituent are numbered as follows:



Compound **5**: IR (THF, cm^{-1}): ν(CO) = 2048 m, 1960 w, 1918 vs, 1895 s. ^1H NMR (400 MHz, [d_6]-acetone): $\delta = 0.80$ (s, 3H, H_7), 0.84 (s, 6H, $H_9 + H_{10}$), 1.01 (m, 1H, H_4), 1.16 (m, 1H, H_5), 1.29 (m, 1H, H_5), 1.68 (m, 2H, H_2), 1.98 (m, 1H, H_3), 2.40 (m, 1H, H4), 3.64 (s, 3H, NCH_3), 3.87 (s, 3H, NCH_3), 4.51 (m, 1H, H_1), 5.73 (s, 1H, $C_\beta H$). ^{13}C NMR (100 MHz, [d_6]-acetone): $\delta = 13.8$ (C_7), 19.1 (C_9), 19.9 (C_{10}), 27.4 (C_4), 28.4 (C_5), 32.0 (NCH_3), 36.8 (NCH_3), 37.6 (C_2), 45.7 (C_3), 48.7 (C_8), 50.3 (C_6), 88.2 (C_1), 102.4 (C_β), 156.0 (C_γ), 189.9 (C_α), 220.3 (*cis*-CO), 224.3 (*trans*-CO). MS (EI), *m*/*z* (%): 440 (15) [M^+], 328 (98) [$(M-4CO)^+$], 300 (100) [$(M-5CO)^+$]. Anal. Calc. for $C_{20}H_{24}N_2O_6Cr$ (440.42): C, 54.54; H, 5.49; N, 6.36. Found: C, 54.72; H, 5.55; N, 6.25%.

Compound **6**: IR (THF, cm^{-1}): ν(CO) = 2080 m, 1973 w, 1933 vs, 1914 m; ν(CCC) = 2006 m. ^1H NMR (400 MHz, [d_6]-acetone): $\delta = 0.80$–0.86 (br, 18H, $H_7+H_9+H_{10}$), 1.10–1.31 (m, 6H, H_4+H_5), 1.65 (m, 4H, H_2), 1.93 (m, 2H, H_3), 2.40–2.50 (m, 2H, H4), 3.28 (s, 3H, $2NCH_3$), 3.47 (br, 9H, NCH_3), 5.26, 5.72 (m, 2H, H_1). ^{13}C NMR (100 MHz, [d_6]-acetone): $\delta = 13.7$ (C_7), 18.9 (C_9), 19.8 (C_{10}), 27.7, 27.9 (C_4), 28.3 (C_5), 35.9, 36.1 (NCH_3), 36.8 ($N(H)CH_3$), 37.1, 37.3 (C_2), 40.6 ($N(H)CH_3$), 45.5 (C_3), 48.8, 48.9 (C_8), 50.1 (C_6), 91.8, 91.9 (C_1), 101.9, 102.4 (C_β), 148.3, 148.5 (C_γ), 198.9, 199.1 (C_α), 218.7 (*cis*-CO), 218.7, 220.3 (*trans*-CO). MS (EI), *m*/*z* (%): 440 (19) [M^+], 328 (100) [$(M-4CO)^+$], 300 (95) [$(M-5CO)^+$]. Anal. Calc. for $C_{20}H_{24}N_2O_6Cr$ (440.42): C, 54.54; H, 5.49; N, 6.36. Found: C, 54.65; H, 5.90; N, 6.30%.

3.4. Pentacarbonyl(1,1-dimethyl-3-phenyl-pyrazolium-5-ylidene)chromium (7)

At room temperature 0.9 ml (1.1 mmol) of 1,1-dimethylhydrazine was added to a solution of 0.35 g (1 mmol) of **1** in 5 ml of THF. The mixture was warmed to 50 °C. The progress of the reaction was monitored by TLC and IR-spectroscopy. After 1 h all of the starting material was consumed. The solvent was removed in vacuo and the residue

was purified by chromatography on silica gel at −20 °C using mixtures of pentane/CH_2Cl_2 (increasing polarity from 3:1 to 1:1) as eluent. The first yellow fraction contained complex **3** (83 mg; 0.21 mmol; 21%). From the second yellow fraction complex **7** (0.27 g, 0.75 mmol; 75%) was obtained after removal of the solvent in vacuo as a yellow solid.

M.p. 88–90 °C (dec.). IR (THF, cm^{-1}): ν(CO) = 2052 m, 1967 w, 1932 vs, 1915 vs, 1901 s. ^{1}H NMR (400 MHz, [d_6]-acetone): δ = 3.27 (s, 6H, 2NCH_3), 6.83 (s, 1H, $C_\beta H$), 7.48 (t, $^3J_{HH}$ = 7.4 Hz, 2H, ArH), 7.58 (t, $^3J_{HH}$ = 7.4 Hz, 1H, ArH), 7.88 (d, $^3J_{HH}$ = 7.4 Hz, 2H, ArH). ^{13}C NMR (100 MHz, [d_6]-acetone): δ = 50.6 (NCH_3), 127.8 (C_β), 128.0, 128.5, 129.1, 132.5 (4 ArC), 169.8 (C_γ), 218.6 (*cis*-CO), 222.8 (*trans*-CO), 234.4 (C_α). MS (EI), *m*/*z* (%): 364 (17) [M^+], 252 (21) [$(M-4CO)^+$], 224 (100) [$(M-5CO)^+$]. UV–Vis (λ_{max}/nm) ($\log\varepsilon$) [CH_2Cl_2]: 402 (3.945). Anal. Calc. for $C_{16}H_{12}N_2O_5Cr$ (364.28): C, 52.76; H, 3.32; N, 7.69. Found: C, 52.90; H, 3.59; N, 7.68%.

3.5. Pentacarbonyl{1-dimethylamine-3-ethyl(methyl)amine-3-phenyl-prop-2-en-1-ylidene}chromium (9)

The reaction of 0.9 ml (1.1 mmol) of 1,1-dimethylhydrazine with a solution of 0.36 g (1 mmol) of **8** in 5 ml of THF was carried out analogously to 3.4 (reaction time: 5 h). Chromatography at −20 °C with pentane/CH_2Cl_2 (increasing polarity from 3:1 to 1:1) first gave a yellow band containing **6** (0.28 g, 0.68 mmol; 68%) and then a second yellow fraction containing compound **9** (70 mg; 0.19 mmol; 19%).

Yellow crystals. M.p. 65–67 °C. IR (THF, cm^{-1}): ν(CO) = 2045 m, 1967 w, 1920 vs, 1903 sh. ^{1}H NMR (400 MHz, [d_6]-acetone): δ = 0.82 (t, $^3J_{HH}$ = 7.0 Hz, 3H, NCH_2CH_3), 2.20 (s, 3H, NCH_3), 2.33 (s, 3H, NCH_3), 2.30–2.44 (m, 2H, NCH_2CH_3), 2.91 (s, 3H, NCH_3), 5.78 (s, 1H, $C_\beta H$), 7.16 (m, 2H, ArH), 7.26 (m, 3H, ArH). ^{13}C NMR (100 MHz, [d_6]-acetone): δ = 11.8 (NCH_2CH_3), 38.1 (NCH_3), 46.4 (NCH_3), 48.0 (NCH_3), 50.6 (NCH_2CH_3), 119.7 (C_β), 129.3, 129.6, 129.9, 138.2 (4 ArC), 143.2 (C_γ), 219.4 (*cis*-CO), 224.7 (*trans*-CO), 257.9 (C_α). MS (EI), *m*/*z* (%): 408 (3) [M^+], 380 (19) [$(M-CO)^+$], 324 (87) [$(M-3CO)^+$], 296 (65) [$(M-4CO)^+$], 268 (100) [$(M-5CO)^+$]. UV–Vis (λ_{max}/nm) ($\log\varepsilon$) [CH_2Cl_2]: 341 (3.889). Anal. Calc. for $C_{19}H_{20}N_2O_5Cr$ (408.38): C, 55.88; H, 4.94; N, 6.86. Found: C, 55.89; H, 4.94; N, 6.96%.

3.6. Pentacarbonyl(4-phenyl-1,5,5a,6,7,8,9,9a-octahydro-benzo-[1,4b]-diazepin-2-ylidene)chromium (10) and N,N′-bis[pentacarbonyl(1′-phenyl-1′,2′-propadienylidene)-chromium]-1,2-diaminocyclohexane (11)

At room temperature 2.28 g (20 mmol) of 1,2-diaminocyclohexane was added to a solution of 0.35 g (1 mmol) of **1** in 5 ml of THF. The progress of the reaction was monitored by TLC. After 60 min all of the starting material was consumed. The solvent was removed in vacuo and the residue chromatographed on silica at −20 °C with mixtures of pentane/CH_2Cl_2/acetone (increasing polarity from 2:1:0 to 4:2:1). The first yellow fraction was collected and the solvent removed in vacuo yielding 0.13 g (0.31 mmol; 31%) of complex **10** as a yellow oil. The second deep-violet fraction containing allenylidene complex **11** (0.10 g, 0.28 mmol; 28%) was obtained as a violet oil.

Compound **10**: IR (THF, cm^{-1}): ν(CO) = 2044 m, 1956 vw, 1918 vs, 1896 sh. ^{1}H NMR (400 MHz, [d_6]-acetone): δ = 0.74 (m, 1H, Hexyl-H), 1.16 (m, 1H, Hexyl-H), 1.43 (m, 1H, Hexyl-H), 1.65–1.67 (m, 4H, Hexyl-H), 3.49 (m, 1H, Hexyl-H), 3.76 (m, 1H, HexylH), 3.92 (m, 1H, Hexy-H), 5.82 (s, 1H, $C_\beta H$), 7.31–7.50 (m, 5H, ArH). ^{13}C NMR (100 MHz, [d_6]-acetone): δ = 15.8 (Hexyl-C), 17.9 (Hexyl-C), 26.3 (Hexyl-C), 26.7 (Hexyl-C), 55.0 (Hexyl-C), 68.3 (Hexyl-C), 100.4 (C_β), 128.4, 129.4, 131.0, 140.6 (4 ArC), 156.9 (C_γ), 220.7 (*cis*-CO), 224.7 (*trans*-CO), 249.2 (C_α). MS (FAB), *m*/*z* (%): 418 (37) [$(M)^+$], 390 (68) [$(M-CO)^+$], 362 (57) [$(M-2CO)^+$], 334 (59) [$(M-3CO)^+$], 306 (84) [$(M-4CO)^+$], 278 (100) [$(M-5CO)^+$]. UV–Vis (λ_{max}/nm) ($\log\varepsilon$) [CH_2Cl_2]: 341 (4.003), 395 (3.854). $C_{20}H_{18}N_2O_5Cr$ (418.37).

Compound **11**: IR (THF, cm^{-1}): ν(CO) = 2078 vw, 1936 vs, 1913 m; ν(CCC) = 1994 m. ^{1}H NMR (400 MHz, [d_6]-acetone): δ = 1.52 (m, 2H, Hexyl-H), 1.65 (m, 2H, Hexyl-H), 1.89 (m, 2H, Hexyl-H), 2.59 (m, 2H, Hexyl-H), 4.82 (m, 2H, Hexyl-H), 7.45 (t, $^3J_{HH}$ = 7.4 Hz, 2H, ArH), 7.50 (t, $^3J_{HH}$ = 7.2 Hz, 2H, ArH), 7.93 (d, $^3J_{HH}$ = 7.4 Hz, 4H, ArH), 10.73 (br, 1H, NH). ^{13}C NMR (100 MHz, [d_6]-acetone): δ = 25.0 (Hexyl-C), 31.8 (Hexyl-C), 62.3 (Hexyl-C), 120.3 (C_β), 129.9, 130.1, 133.5, 134.8 (4 ArC), 153.0 (C_γ), 218.6 (*cis*-CO), 219.3 (C_α), 224.0 (*trans*-CO). MS (FAB), *m*/*z* (%): 722 (11) [$(M)^+$], 638 (39) [$(M-3CO)^+$], 532 (75) [$(M-5CO)^+$], 526 (43) [$(M-7CO)^+$], 470 (92) [$(M-9CO)^+$], 442 (100) [$(M-10CO)^+$]. Anal. Calc. for $C_{34}H_{22}N_2O_{10}Cr_2$ (722.55): C, 56.52; H, 3.07; N, 3.88. Found: C, 56.54; H, 3.88; N, 3.99%.

3.7. Pentacarbonyl(1,2,3,4-tetrahydro-5-phenyl-1,4-thiazepin-7-ylidene)chromium (12)

At room temperature 1.54 g (20 mmol) of 2-mercaptoethylamine were added to a solution of 0.35 g (1 mmol) of **1** in 5 ml of THF. When all of the starting material (control by IR-spectroscopy) was consumed the solvent was removed in vacuo and the residue purified by chromatography on silica at −20 °C using mixtures of pentane/CH_2Cl_2 (increasing polarity from 2:1 to 1:1) as eluent. The deep violet fraction was collected yielding 0.33 g (0.87 mmol; 87%) of complex **12** as a violet solid.

M.p. 114–116 °C. IR (THF, cm^{-1}): ν(CO) = 2044 m, 1962 vw, 1924 vs, 1901 sh. ^{1}H NMR (400 MHz, [d_6]-acetone): δ = 3.29 (m, 2H, NCH_2CH_2S), 4.01 (m, 2H, NCH_2CH_2S), 7.32 (s, 1H, $C_\beta H$), 7.42 (t, $^3J_{HH}$ = 7.4 Hz, 2H, ArH), 7.49 (t, $^3J_{HH}$ = 7.4 Hz, 1H, ArH), 7.61 (d, $^3J_{HH}$ = 7.4 Hz, 2H, ArH), 8.93 (br, 1H, NH). ^{13}C NMR (100 MHz, [d_6]-acetone): δ = 48.9 (SCH_2CH_2N), 50.4 (SCH_2CH_2N), 123.3 (C_β), 129.2, 129.8, 132.6, 138.7 (4

ArC), 157.7 (C_γ), 219.9 (*cis*-CO), 226.1 (*trans*-CO), 270.9 (C_α). MS (FAB), *m/z* (%): 381 (21) [M^+], 353 (64) [$(M-CO)^+$], 325 (48) [$(M-2CO)^+$], 297 (28) [$(M-3CO)^+$], 269 (100) [$(M-4CO)^+$], 251 (68) [$(M-5CO)^+$]. UV–Vis (λ_{max}/nm) ($\log\varepsilon$) [solvent]: 383 (3.760), 563 (3.658) [pentane], 384 (4.158), 513 (4.083) [CH_2Cl_2], 384 (4.153), 524 (4.010) [$CHCl_3$], 378 (4.076), 465 (3.964) [DMF]. Anal. Calc. for $C_{16}H_{11}NO_5SCr$ (381.33): C, 50.40; H, 2.91; N, 3.67. Found: C, 50.42; H, 2.83; N, 3.56%.

3.8. Pentacarbonyl(1,2,3,4-tetrahydro-2-(*R*)-methoxycarbonyl-7-phenyl-1,4-thiazepine-5-ylidene)chromium (**13**) and pentacarbonyl(1,2,3,4-tetrahydro-2-(*R*)-ethoxycarbonyl-7-phenyl-1,4-thiazepine-5-ylidene)chromium (**14**)

At room temperature 20 mmol of an aqueous solution of 2-(*R*)-amino-3-mercapto-propyonic acid methylester or 2-(*R*)-amino-3-mercapto-propyonic acid ethylester (both 97% enantiomerically pure and prepared in situ by adding an equimolar amount of a concentrated NaOH solution to the corresponding hydrochlorides) was added to a solution of 0.35 g (1 mmol) of **1** in 5 ml of THF. When all of the starting material was consumed (IR control) the solvent was removed in vacuo and the residue chromatographed on silica at −20 °C with pentane/CH_2Cl_2 (increasing polarity from 1:1 to 1:3). The deep violet fraction was collected and the solvent removed in vacuo yielding 0.30 g (0.69 mmol; 69%) of complex **13** [0.33 g (0.72 mmol; 72%) of compound **14**] as a violet solids. Both samples contained small amounts of the corresponding *S*-enantiomer.

Compound **13**: M.p. 98–100 °C. IR (THF, cm^{-1}): ν(CO) = 2045 m, 1965 vw, 1928 vs, 1904 sh. ^{1}H NMR (400 MHz, [d_6]-acetone): δ = 3.56 (m, 2H, S*C*H_2CHN), 3.69 (s, 3H, $COOCH_3$), 5.10 (m, 1H, SCH_2CHN), 7.38 (s, 1H, C_βH), 7.45 (t, $^3J_{HH}$ = 7.4 Hz, 2H, ArH), 7.50 (t, $^3J_{HH}$ = 7.4 Hz, 1H, ArH), 7.62 (d, $^3J_{HH}$ = 7.4 Hz, 2H, ArH), 8.64 (br, 1H, NH). ^{13}C NMR (100 MHz, [d_6]-acetone): δ = 49.5 (S*C*H_2CHN), 53.5 (SCH_2*C*HN), 62.1 ($COOCH_3$), 124.7 (C_β), 129.0, 130.0, 132.5, 139.7 (4 ArC), 154.9 (C_γ), 168.7 (*C*$OOCH_3$), 219.6 (*cis*-CO), 226.4 (*trans*-CO), 278.4 (C_α). MS (FAB), *m/z* (%): 439 (9) [$(M+H)^+$], 411 (33) [$(M-CO+H)^+$], 355 (37) [$(M-3CO+H)^+$], 327 (38) [$(M-4CO+H)^+$], 299 (100) [$(M-5CO+H)^+$]. UV–Vis (λ_{max}/nm) ($\log\varepsilon$) [solvent]: 383 (3.924), 567 (3.899) [pentane], 383 (4.189), 525 (4.016) [CH_2Cl_2], 383 (3.903), 539 (4.001) [$CHCl_3$], 377 (3.993), 477 (3.870) [DMF]. Anal. Calc. for $C_{18}H_{13}NO_7SCr$ (438.36): C, 49.21; H, 2.98; N, 3.19. Found: C, 49.73; H, 3.15; N, 3.21%.

Compound **14**: M.p. 87–89 °C. IR (THF, cm^{-1}) ν(CO): 2045 m, 1965 vw, 1927 vs, 1905 sh. ^{1}H NMR (400 MHz, [d_6]-acetone): δ = 1.18 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $COOCH_2$-*C*H_3), 3.55 (m, 2H, S*C*H_2CHN), 4.14 (q, $^3J_{HH}$ = 7.4 Hz, 2H, $COOCH_2CH_3$), 5.08 (m, 1H, SCH_2CHN), 7.39 (s, 1H, C_βH), 7.45–7.50 (m, 3H, ArH), 7.63 (d, $^3J_{HH}$ = 7.4 Hz, 2H, ArH), 8.66 (br, 1H, NH). ^{13}C NMR (100 MHz, [d_6]-acetone): δ = 14.3 ($COOCH_2CH_3$), 49.2 (S*C*H_2CHN), 62.0 (SCH_2*C*HN), 68.0 ($COOCH_2CH_3$), 124.6 (C_β), 129.0, 129.9, 132.4, 139.8 (4 ArC), 154.9 (C_γ), 168.1 (*C*$OOCH_2CH_3$), 219.5 (*cis*-CO), 226.3 (*trans*-CO), 277.9 (C_α). MS (FAB), *m/z* (%): 453 (45) [$(M)^+$], 425 (33) [$(M-CO)^+$], 369 (34) [$(M-3CO)^+$], 341 (100) [$(M-4CO)^+$], 313 (68) [$(M-5CO)^+$]. UV–Vis (λ_{max}/nm) ($\log\varepsilon$) [CH_2Cl_2]: 383 (4.181), 523 (4.065). Anal. Calc. for $C_{19}H_{15}NO_7SCr$ (453.39): C, 50.33; H, 3.33; N, 3.09. Found: C, 50.37; H, 3.58; N, 3.13%.

3.9. Pentacarbonyl(1,6,7,8-tetrahydro-6-methoxycarbonyl-2-phenyl-4H-1,5-thiazocane-4-ylidene)chromium (**15**)

2.98 g (20 mmol) of a freshly prepared racemic mixture of 2-amino-4-mercapto-butyric acid methylester were added at room temperature to a solution of 0.35 g (1 mmol) of **1** in 5 ml of THF. After completion of the reaction (IR control) the solvent was removed in vacuo and the residue purified by chromatography on silica at −20 °C using pentane/CH_2Cl_2 (increasing polarity from 1:1 to 1:3) as eluent. The deep violet fraction gave 0.31 g (0.69 mmol; 69%) of complex **15** as a violet solid.

M.p. 84–86 °C. IR (THF, cm^{-1}): ν(CO) = 2044 m, 1964 vw, 1928 vs, 1903 sh. ^{1}H NMR (400 MHz, [d_6]-acetone): δ = 1.92 (m, 1H, SCH_2CH_2CHN), 2.13 (m, 1H, SCH_2CH_2CHN), 2.93 (m, 1H, S*C*H_2CH_2CHN), 3.59 (m, 1H, S*C*H_2CH_2CHN), 3.81 (s, 3H, $COOCH_3$), 5.19 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 3.8 Hz, 1H, SCH_2CHN), 7.01 (s, 1H, C_βH), 7.55 (t, $^3J_{HH}$ = 7.1 Hz, 2H, ArH), 7.65 (t, $^3J_{HH}$ = 7.2 Hz, 1H, ArH), 7.76 (d, $^3J_{HH}$ = 7.2 Hz, 2H, ArH), 8.12 (br, 1H, NH). ^{13}C NMR (100 MHz, [d_6]-acetone): δ = 22.8 (SCH_2CH_2CHN), 39.1 (S*C*H_2CH_2CHN), 53.4 (SCH_2CH_2*C*HN), 57.8 ($COOCH_3$), 120.0 (C_β), 129.8, 130.0, 133.7, 137.7 (4 ArC), 158.3 (C_γ), 171.1 (*C*$OOCH_3$), 219.8 (*cis*-CO), 226.3 (*trans*-CO), 276.9 (C_α). MS (FAB) *m/z* (%): 453 (6) [$(M)^+$], 425 (27) [$(M-CO)^+$], 389 (100) [$(M-COOCH_3)^+$], 369 (25) [$(M-3CO)^+$], 341 (41) [$(M-4CO)^+$], 313 (71) [$(M-5CO)^+$]. UV–Vis (λ_{max}/nm) ($\log\varepsilon$) [solvent]: 410 (3.891), 556 (3.987) [pentane], 411 (3.967), 527 (4.052) [CH_2Cl_2], 412 (4.011), 537 (4.090) [$CHCl_3$], 382 (3.911), 485 (3.920) [DMF]. Anal. Calc. for $C_{19}H_{15}NO_7SCr$ (453.29): C, 50.34; H, 3.36; N, 3.09. Found: C, 50.44; H, 3.80; N, 2.83%.

3.10. Photochemical generation of the tetracarbonyl(phosphine)carbene complexes **16** and **17**

A solution of 1 mmol of the carbene complexes **2** and **12** and 0.29 g (1.1 mmol) of triphenylphosphine in 30 ml of dry THF was irradiated at −30 °C for ca. 2 h while passing a slow stream of argon through the solution. The progress of the reaction was monitored by IR-spectroscopy. When all of the starting material was consumed the solvent was removed in vacuo and the residue chromatographed on silica gel at −20 °C with pentane/CH_2Cl_2 (increasing polarity from 2:1 to 1:2). The fractions containing the product

complexes were collected and the solvent removed in vacuo yielding 0.52 g (0.87 mmol; 87%) of complex **16** as a yellow solid and 0.36 g (0.59 mmol; 59%) of complex **17** as a violet solid.

3.11. Tetracarbonyl(triphenylphosphine)(1,2-dimethyl-3-phenyl-pyrazol-5-ylidene)chromium (**16**)

M.p. 124–126 °C. IR (THF, cm^{-1}) ν(CO): 1991 s, 1892 s, 1869 vs, 1848 s. ^1H NMR (400 MHz, [d_6]-acetone): $\delta = 3.64$ (s, 3H, NCH_3), 3.87 (s, 3H, NCH_3), 5.88 (s, 1H, $C_\beta H$), 7.12–7.33 (m, 20H, ArH). ^{13}C NMR (100 MHz, [d_6]-acetone): $\delta = 38.2$ (NCH_3), 38.3 (NCH_3), 121.9 (d, $^3J_{PC} = 2.8$ Hz, C_β), 128.7 (d, $^3J_{PC} = 8.6$ Hz, PArC), 129.6 (d, $^4J_{PC} = 1.9$ Hz, PArC), 129.6, 129.7, 129.8, 130.0 (4 ArC), 134.0 (d, $^2J_{PC} = 11.5$ Hz, PArC), 137.9 (d, $^1J_{PC} = 27.7$ Hz, PArC), 197.4 (d, $^2J_{PC} = 14.3$ Hz, C_α), 224.3 (d, $^2J_{PC} = 13.4$ Hz, *cis*-CO), 228.8 (d, $^2J_{PC} = 12.5$ Hz, *trans*-CO), 231.1 (*cis*-$CO_{trans\ to\ P}$). ^{31}P NMR (162 MHz, d_6-acetone): $\delta = 60.8$. MS (FAB), *m*/*z* (%): 486 (100) [$(M-4CO)^+$]. UV–Vis (λ_{max}/nm) ($\log\varepsilon$) [CH_2Cl_2]: 384 (3.945). Anal. Calc. for $C_{33}H_{27}N_4O_5PCr$ (598.56): C, 66.22; H, 4.55; N, 4.68. Found: C, 66.15; H, 4.53; N, 4.75%.

3.12. Tetracarbonyl(triphenylphosphine)(1,2,3,4-tetrahydro-5-phenyl-1,4-thiazepin-7-ylidene)chromium (**17**)

M.p. 84–86 °C (dec.). IR (THF, cm^{-1}): ν(CO) = 1989 s, 1898 s, 1879 vs, 1864 sh. ^1H NMR (400 MHz, [d_6]-acetone): $\delta = 3.06$ (m, 2H, NCH_2CH_2S), 3.59 (m, 2H, NCH_2CH_2S), 7.20–7.48 (m, 21H, $C_\beta H$+ArH), 8.12 (br, 1H, NH). ^{13}C NMR (100 MHz, [d_6]-acetone): $\delta = 49.3$ (SCH_2CH_2N), 50.0 (SCH_2CH_2N), 124.7 (C_β), 128.6 (d, $^2J_{PC} = 8.7$ Hz, PArC), 128.9 (ArC), 129.4 (ArC), 130.0 (br, PArC), 131.6 (ArC), 134.1 (d, $^2J_{PC} = 10.6$ Hz, PArC), 137.4 (d, $^2J_{PC} = 28.8$ Hz, PArC), 139.7 (ArC), 152.6 (C_γ), 222.7 (d, $^2J_{PC} = 14.5$ Hz, *cis*-CO), 230.6 (*cis*-$CO_{trans\ to\ P}$), 232.0 (d, $^2J_{PC} = 7.7$ Hz, *trans*-CO), 257.4 (d, $^2J_{PC} = 7.7$ Hz, C_α). ^{31}P NMR (162 MHz, d_6-acetone): $\delta = 59.7$. MS (FAB), *m*/*z* (%): 615 (13) [M^+], 587 (31) [$(M-CO)^+$], 531 (100) [$(M-3CO)^+$], 503 (69) [$(M-4CO)^+$]. UV–Vis (λ_{max}/nm) ($\log\varepsilon$) [solvent]: 389 (3.935), 571 (3.757) [CH_2Cl_2], 387 (3.900), 580 (3.742) [Et_2O], 389 (3.915), 565 (3.754) [THF], 387 (3.928), 547 (3.730) [acetone], 387 (3.918), 536 (3.738) [DMF]. Anal. Calc. for $C_{33}H_{26}NO_5PSCr$ (615.60): C, 64.39; H, 4.26; N, 2.28. Found: C, 64.39; H, 4.09; N, 2.26%.

3.13. X-ray structural analyses of **2**, **7**, **14**, **15** and **16**

Single crystals suitable for X-ray structural analyses were obtained by slow diffusion at 4 °C of *n*-hexane into solutions of **2**, **7**, **14**, **15** and **16** in CH_2Cl_2. The *R*:*S* ratio of 2-amino-3-mercapto-propyonic acid ethylester used in the synthesis of **14** was 3:97. After chromatography, *n* the fraction selected for the crystallization experiments, the *R*:*S* ratio had increased to 8:92. The solubility of racemic **14** is less than that of enantiomerically pure **14** and thus, by accident, a crystal of racemic **14** was used for the X-ray structural analysis.

The measurements were performed with a crystal mounted on a glass fibre on a Siemens P4 diffractometer (graphite

Table 1
Crystal data and refinement details for compounds **2**, **7** and **14**

Compound	**2**	**7**	**14**
Formula	$C_{16.5}H_{13}ClCrN_2O_5$	$C_{16}H_{12}CrN_2O_5$	$C_{19}H_{15}CrNO_7S$
Molecular weight	406.74	364.28	453.39
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$	*C*2/*c*
a (Å)	24.987(10)	11.019(4)	27.557(8)
b (Å)	7.699(4)	9.807(3)	8.949(3)
c (Å)	19.104(8)	15.948(5)	21.085(6)
α (°)	90	90	90
β (°)	103.49(3)	103.87(3)	128.38(3)
γ (°)	90	90	90
V (Å^3)	3574(3)	1673.1(9)	4076(2)
Z	8	4	8
Crystal size (mm^3)	$0.5 \times 0.4 \times 0.3$	$0.3 \times 0.3 \times 0.2$	$0.5 \times 0.4 \times 0.3$
ρ_{calc} (g cm^{-3})	1.515	1.446	1.438
μ (mm^{-1})	0.819	0.711	0.702
F(000)	1656	744	1808
T (K)	188(2)	188(2)	188(2)
Maximum 2Θ (°)	54	54	54
Index range	$-31 \leqslant h \leqslant 31$, $-9 \leqslant k \leqslant 9$, $-24 \leqslant l \leqslant 24$	$-14 \leqslant h \leqslant 14$, $-9 \leqslant k \leqslant 12$, $-20 \leqslant l \leqslant 20$	$-35 \leqslant h \leqslant 35$, $-11 \leqslant k \leqslant 11$, $-26 \leqslant l \leqslant 26$
Number of data	7237	4249	8569
Number of unique data	3911	3625	4466
Parameters	231	217	265
$R(F)$ for $I > 2\sigma > (I)$	0.1026	0.0497	0.0582
$wR_2(F^2)$ for all data	0.2034	0.1390	0.1308
Goodness-of-fit on F^2	1.066	1.023	1.026

Table 2
Crystal data and refinement details for compounds **15** and **16**

Compound	**15**	**16**
Formula	$C_{19}H_{15}CrNO_7S$	$C_{33}H_{27}CrN_2O_4P$
Molecular weight	453.38	598.54
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	10.012(3)	14.056(3)
b (Å)	10.103(3)	14.454(3)
c (Å)	10.487(5)	14.302(3)
α (°)	93.83(2)	90
β (°)	101.08(3)	92.56(3)
γ (°)	98.490(8)	90
V (Å^3)	1024.6(6)	2902.7(10)
Z	2	4
Crystal size (mm^3)	$0.5 \times 0.4 \times 0.3$	$0.3 \times 0.25 \times 0.2$
ρ_{calc} (g cm^{-3})	1.470	1.370
μ (mm^{-1})	0.700	0.490
$F(000)$	464	1240
T (K)	188(2)	100(2)
Maximum 2Θ (°)	54	58
Index range	$-12 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $-13 \leqslant l \leqslant 13$	$-19 \leqslant h \leqslant 19$, $-19 \leqslant k \leqslant 16$, $-16 \leqslant l \leqslant 19$
Number of data	5885	24385
Number of unique data	4475	7756
Parameters	262	370
$R(F)$ for $I > 2\sigma > (I)$	0.0594	0.0552
$wR_2(F^2)$ for all data	0.1599	0.1165
Goodness-of-fit on F^2	1.021	1.026

monochromator, Mo Kα, radiation, $\lambda = 0.71073$ Å). For the data collection the Wykhoff technique was used. Semi-empirical absorption correction (ψ scan with 12 reflections) was performed. Crystal data and refinement details are compiled in Tables 1 and 2. The structures were solved by direct methods using the SHELXTL-97 program package [31]. The positions of the hydrogen atoms were calculated by assuming ideal geometry, and their coordinates were refined together with those of the attached carbon atoms as riding-model. All other atoms were refined anisotropically.

Acknowledgements

Support of these investigations by the Wacker-Chemie GmbH (gift of chemicals) is gratefully acknowledged. G.G.M. thanks the Alexander-von-Humboldt Foundation for a grant.

Appendix A. Supplementary material

CCDC 608559, 608560, 608561, 608562 and 608563 contain the supplementary crystallographic data for **2**, **7**, **13**, **15** and **16**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.07.049.

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