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The first pyrazole molybdenum(0) complexes: *cis*-[Mo(CO)$_4$(Hdmpz)$_2$] crystallizes as a N–H···OC hydrogen-bonded dimer

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Abstract

The reactions of [Mo(CO)$_4$(NBD)] with two equivalents of Hpz (pyrazole) or Hdmpz (3,5-dimethylpyrazole) in hexane lead to the precipitation of *cis*-[Mo(CO)$_4$(Hpz)$_2$] or *cis*-[Mo(CO)$_4$(Hdmpz)$_2$], which are the first pyrazole complexes of molybdenum(0). In the solid state structure of *cis*-[Mo(CO)$_4$(Hdmpz)$_2$], two molecules are self-assembled by intermolecular hydrogen bonds between the N-bound hydrogen of one Hdmpz ligand and a oxygen atom of a carbonyl group. This explains the lack of planarity observed for the nitrogen donor atom of the Hdmpz involved in the intermolecular interaction. The complexes are unstable in solution and as solids.

Keywords: Molybdenum; Pyrazoles; Carbonyls; Hydrogen bonds

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1. Introduction

Complexes containing pyrazole ligands present several aspects of main interest. Concerning their crystal structure, the N-bound hydrogen of pyrazole complexes is commonly involved in hydrogen-bonds, giving rise to supramolecular arrangements which are related to one of the big challenges of chemistry, that is the understanding and control of the organization of molecules [1]. Uncoordinated pyrazoles lead to chains, or cyclic oligomers in the solid state, depending on the nature of their substituents [2]. Pyrazole complexes, however, frequently exhibit intramolecular hydrogen bonds, or hydrogen bonding to solvent molecules or counterions in their crystal structures. In contrast, they rarely show intermolecular hydrogen-bonded chains or oligomers [3,4].

A second aspect of interest concerns their reactivity. Terminal pyrazole ligands are very useful precursors for homo- or heterobimetallic complexes, which may be obtained by deprotonating the N-bound hydrogen of the coordinated pyrazole when a second metallic substrate is present (Scheme 1). This strategy has been successively used by different groups, mainly with middle and late transition elements [5].

We have recently reported the synthesis of (allyl)molybdenum(II) complexes containing two terminal pyrazoles coordinated *cis*, and their use as precursors for heterobimetallic molybdenum–gold complexes [6]. We considered of interest to explore the chemistry of similar molybdenum(0) complexes containing two terminal pyrazoles coordinated *cis*. These species had not been previously reported, as opposite to the similar chromium(0) and tungsten(0) complexes with 3,5-dimethylpyrazole, which were reported 30 years ago [7]. The syntheses, structure, and chemical behavior of these complexes are herein described.

2. Results and discussion

The reactions of [Mo(CO)$_4$(NBD)] with two fold excess of pyrazole (Hpz) or dimethylpyrazole (Hdmpz) in hexane occur rapidly at room temperature, leading to the precipitation of *cis*-[Mo(CO)$_4$(Hpz)$_2$] (**1**) or *cis*-

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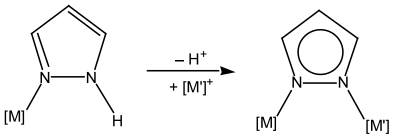

Scheme 1.

$[Mo(CO)_4(Hdmpz)_2]$ (**2**), respectively, isolated as yellow microcrystalline solids. The reaction is faster for Hpz, what can be attributed to steric reasons.

The *cis* geometry of both complexes is evident from their solid IR spectra in the C–O stretching region, which show four absorptions. The C–O frequencies are slightly higher for **1** than for **2**, as is to be expected considering that Hdmpz is a better donor than Hpz.

No structures of pyrazoles coordinated to Group 6 metals in oxidation state zero had been previously reported, therefore the geometry of **2** was subjected to an X-ray diffractometric study. Although several structures of *cis*-tetracarbonyl complexes containing chelating ligands derived from pyrazoles have been reported [8], structure reports of pyrazole molybdenum complexes are relatively scarce, and the metal has a high oxidation state in most of them [6,9]. On the other hand, there are many structure reports of tetracarbonylmolybdenum(0) complexes containing a chelate nitrogen donor ligand, but we have found only one precedent of a similar structure containing two monodentate nitrogen donor ligands [10].

The structure obtained is shown in Fig. 1 and relevant distances and angles are collected in Table 1. The octahedral geometry is severely distorted, as is usually observed in other tetracarbonyl complexes containing nitrogen donor ligands. This is clearly shown by the deviation from the linearity of the *trans* carbonyl groups (170.82(11)°). The nitrogen donor atoms and the *trans* carbonyls are also slightly deviated from linearity (175.91(9) and 176.53(9)°). Slight distortions are also observed for the mutually *cis*-carbonyl groups (*cis*-C–Mo–C angles range from 85.14(11) to 87.92(11)°) and for the carbonyls *cis* to Hdmpz (*cis*-N–Mo–C angles range from 90.81(9) to 97.81(10)°). The angle formed by the two Hdmpz ligands is also lower than 90° (86.25(7)°). A similar value (85.4(2)°) is detected in the only precedent suitable for comparison, that is *cis*-$[Cr(CO)_4py_2]$ [11], where a Group 6 metal in oxidation state zero is coordinated to two monodentate nitrogen donor ligands, these being pyridines, which resemble closely the pyridinic nitrogen of pyrazole. However, this angle is larger than those found when the pyrazole is a part of a chelating ligand coordinated to molybdenum(0), such as pyrazolylpyridine, pyrazolylpyridazine or bis(pyrazolyl)methane [8]. The Mo–N distances in these complexes are similar to those detected in **2** (2.276(2) and 2.304(2) Å), as well as the N–C and C–C distances in the heterocycles. The Mo–C lengths of the carbonyls *trans* to Hdmpz (1.941(3) and 1.945(3) Å) are shorter than those *cis* to them (2.036(3) and 2.044(3) Å), as a result of the strong donor character of the Hdmpz ligand compared with the carbonyl.

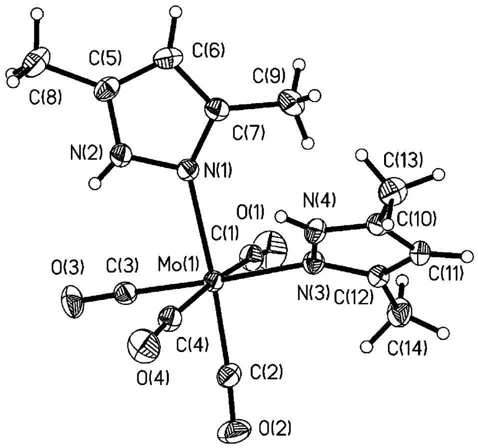

Fig. 1. Perspective view of *cis*-$[Mo(CO)_4(Hdmpz)_2]$ (**2**) showing the atom numbering.

Table 1
Selected distances (Å) and angles (°) for *cis*-$[Mo(CO)_4(Hdmpz)_2]$ (**2**)

Mo(1)–C(3)	1.941(3)
Mo(1)–C(2)	1.945(3)
Mo(1)–C(1)	2.036(3)
Mo(1)–C(4)	2.044(3)
Mo(1)–N(3)	2.276(2)
Mo(1)–N(1)	2.304(2)
N(1)–C(7)	1.338(3)
N(1)–N(2)	1.364(3)
N(2)–C(5)	1.338(4)
N(3)–C(12)	1.333(3)
N(3)–N(4)	1.361(3)
N(4)–C(10)	1.332(3)
C(5)–C(6)	1.368(4)
C(6)–C(7)	1.397(4)
C(10)–C(11)	1.361(4)
C(11)–C(12)	1.398(4)
C(3)–Mo(1)–C(2)	85.14(11)
C(3)–Mo(1)–C(1)	87.92(11)
C(2)–Mo(1)–C(1)	86.39(12)
C(3)–Mo(1)–C(4)	86.77(11)
C(2)–Mo(1)–C(4)	85.71(11)
C(1)–Mo(1)–C(4)	170.82(11)
C(3)–Mo(1)–N(3)	176.53(9)
C(2)–Mo(1)–N(3)	97.81(10)
C(1)–Mo(1)–N(3)	94.08(9)
C(4)–Mo(1)–N(3)	91.62(9)
C(3)–Mo(1)–N(1)	90.81(9)
C(2)–Mo(1)–N(1)	175.91(9)
C(1)–Mo(1)–N(1)	92.92(10)
C(4)–Mo(1)–N(1)	94.63(10)
N(3)–Mo(1)–N(1)	86.25(7)

The N-bound hydrogens of both Hdmpz point to the same side of the molecule, what could be attributed to steric reasons, as this orientation reduces the steric hindrance of the methyl groups. As discussed below, electronic factors cannot be completely ruled out, since the N-bound hydrogens in the structures of these two complexes are involved in moderate or weak intermolecular hydrogen bonds, and therefore they could also be responsible for the orientation of both Hdmpz.

The Hdmpz ligands are tilt in the same sense around the Mo–N bonds, being close to the planes which bisect the angles between *cis* substituents. This feature seems to be common to other heterocyclic nitrogen donor ligands acting as monodentate, as dihedral angles close to 45° have also been found in the structure of *cis*-[Cr(CO)$_4$py$_2$] [11]. In **2**, the averaged dihedral angles are 47(1)° for the Hdmpz ligand containing N(3) as donor atom, but only 29(1)° for the Hdmpz ligand containing N(1). The latter value is smaller than the expected angle, since this nitrogen donor atom is not planar. This is a striking feature considering that the donor atom is a pyridinic nitrogen (see Scheme 1) and should be planar, as occurs in *cis*-[Cr(CO)$_4$py$_2$] [11]. However, in **2** the Mo–N(1) bond is not coplanar with the Hdmpz plane which contains N(1), but bent 16.0(4)°, whereas the Mo–N(3) bond is, as expected, coplanar with its respective Hdmpz plane (the angle between the Mo–N(3) bond and the heterocycle plane is 0.16(3)°).

An examination of the hydrogen bonds involving the N-bound hydrogen of the 'bent' Hdmpz explains this uncommon feature. The shortest intermolecular hydrogen bonds detected is 2.23 Å for H(2)···O(3). This and the corresponding N(2)···O(3) distance (2.988(13) Å) confirm the presence of a hydrogen bond which may be considered as 'moderate' [12]. As shown in Fig. 2, two molecules are linked by complementary two hydrogen bonds, giving a dimeric structure. The bending of the pyrazole favors the intermolecular interaction, as shown in Fig. 2. The other N-bound hydrogen is also involved in intermolecular hydrogen bonds, but these may be considered as 'weak': H(4)···O(2) = 2.55 Å; H(4)···O(4) = 2.64 Å [12], and they are not shown in Fig. 2.

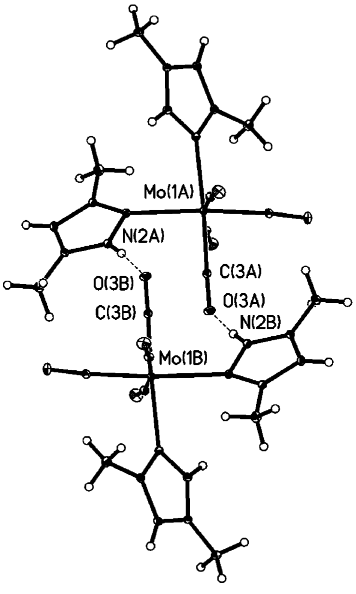

Fig. 2. Perspective view of two molecules of *cis*-[Mo(CO)$_4$(Hdmpz)$_2$] (**2**) linked by NH···OC hydrogen bonds.

The participation of a CO ligand as acceptor in these hydrogen bonds is remarkable, as we have not been able to find any precedent of such an interaction where the donor N–H group belongs to a pyrazole. A growing attention is recently receiving the intermolecular interactions with participation of carbonyls, which are one of the prototype ligands in organometallic chemistry [13]. The presence of this interaction in **2** may be explained considering that the oxygen of the carbonyls are the more basic sites of the molecule, since carbonyls participate in hydrogen bonds only when other acceptors are not in competition. This is confirmed since the carbonyls involved in the hydrogen interaction in the structure of **2** are those *trans* to nitrogen donors, which are more basic [14]. The N(2)···O(3)–C(3) angle is close to 120° (125(1)°), what also points to the basicity of these carbonyls, which increases with their ketonic nature.

The characterization of the complexes in solution is difficult due to their high unstability. Thus, clean ^{1}H-NMR spectra could only be recorded after the solids were mixed with frozen CDCl$_3$ at 195 K, and the NMR spectra were recorded at 253 K immediately after the solvent melted. The spectra show singlets for all the signals of the equivalent pyrazoles, except the N-bound protons of **1**, which display a broad signal. This broadness might be due to a rapid prototropic exchange involving the N-bound proton, which is common in pyrazole complexes [15]. The observation of singlets for the pyrazolic protons of **1** contrasts with the coupling observed for similar molybdenum(II) complexes [6]. The assignment of the pyrazolic hydrogens is tentative, since the chemical shift of the hydrogens or methyl groups in positions 3 and 5 seems to be affected by different factors, which are difficult to evaluate: whether the hydrogen (or methyl) group at position 3 resonates at higher field than 5 or vice versa may vary in the same family of complexes [16], or even depending on the solvent used [17]. Other NMR experiments were precluded by the unstability of the complexes, and also sometimes by their low solublility, as for the ^{13}C-NMR.

The IR spectra of the C–O stretching region show the expected four absorptions for a *cis*-tetracarbonyl, being those of **1** slightly higher, as should be expected. The NMR and IR spectra were examined in order to obtain information about what type of processes occur in solution, and the final products were isolated as solids. However, the only identifiable signals detected in solution were those corresponding to free pyrazole and to $[Mo(CO)_6]$. The solids finally obtained could neither be identified, as they did not show any C–O stretching absorption. Finally, the solids had to be stored under a dinitrogen atmosphere at −20 °C, but even under these conditions **1** darkened and decomposed in a few days. This unstability precluded any study of their reactivity. All the attempts to deprotonate the pyrazoles and further attack of different metallic fragments (Scheme 1) lead to decomposition products. As indicated before, the metal has a high oxidation state in most of the structures previously reported of pyrazole molybdenum complexes, what points to its preference for hard metal centers. Therefore, the unstability of these complexes may be explained considering the hard character of the pyrazole ligands bonded to a soft molybdenum(0) center.

3. Experimental

All manipulations were performed under N_2 atmosphere following conventional Schlenk techniques. Solvents were purified according to standard procedures [18]. $[Mo(CO)_4(NBD)]$ was obtained as previously described [19]. Other reagents were obtained from the usual commercial suppliers, and used as received. Infrared spectra were recorded in Perkin–Elmer RX I FT-IR apparatus on KBr pellets from 4000 to 400 cm^{-1}. NMR spectra were recorded in Bruker AC-300 or ARX-300 instruments in $CDCl_3$. NMR spectra are referred to the internal residual solvent peak for ^1H-NMR spectra. Elemental analyses were performed on a Perkin–Elmer 2400B microanalyzer.

3.1. *$[Mo(CO)_4(Hpz)_2]$ (**1**)*

Hpz (0.068 g, 1.0 mmol) was added to a solution of $[Mo(CO)_4(NBD)]$ (0.150 g, 0.5 mmol) in hexane (20 ml), and the mixture was stirred for 45 min, during which time a microcrystalline yellow solid precipitated. The colorless solution was decanted, and the solid was washed with hexane (3 × 3 ml) and vacuum dried, yielding 0.109 g (63%). IR (THF), ν(CO): 2012 m, 1888 vs, 1877 vs(sh), 1835 s. IR (KBr): 3434 s, 3154 w, 2024 m, 1898 vs, 1844 s, 1779 s, 1630 s, 1522 w, 1463 w, 1402 w, 1350 w, 1263 w, 1118 m, 1050 w, 763 m, 687 w, 652 w, 610 w, 577 w. ^1H-NMR (253 K, 300 MHz): 10.12 (br, HN, 2 H), 7.61 (s, $H^{5,3}$ Hpz, 2 H), 7.36 (s, $H^{3,5}$ Hpz, 2 H), 6.37 (s, H^4 Hpz, 2 H). Anal. Calc. for $C_{10}H_8MoN_4O_4$: C, 34.90; H, 2.34; N, 16.28. Found: C, 35.26; H, 2.27; N, 16.26%.

3.2. *$[Mo(CO)_4(Hdmpz)_2]$ (**2**)*

Hdmpz (0.577 g, 6.0 mmol) was added to a solution of $[Mo(CO)_4(NBD)]$ (0.900 g, 3.0 mmol) in hexane (100 ml), and the mixture was stirred for 9 h, during which time a microcrystalline yellow solid precipitated. The colorless solution was decanted, and the solid was washed with hexane (3 × 5 ml) and vacuum dried, yielding 1.164 g (97%). IR (THF), ν(CO): 2009 m, 1882 vs, 1872 vs(sh), 1833 s. IR (KBr): 3431 m, 3374 m, 2926 w, 2018 m, 1916 s, 1860 vs, 1787 vs, 1575 m, 1421 w, 1376 w, 1282 w, 1155 w, 1040 w, 1022 w, 798 w, 653 w, 616 w, 580 w, 555 w. ^1H-NMR (253 K, 300 MHz): 9.42 (s, HN, 2 H), 5.87 (s, H^4 Hdmpz, 2 H), 2.27 (s, CH_3 Hdmpz, 6 H), 1.98 (s, CH_3 Hdmpz, 6 H). Anal. Calc. for $C_{14}H_{16}MoN_4O_4$: C, 42.01; H, 4.03; N, 14.00. Found: C, 42.28; H, 3.87; N, 13.84%.

3.3. *X-ray crystallographic study of **2***

Crystals were grown by slow diffusion of a solution of Hdmpz in hexane into a solution of $[Mo(CO)_4(NBD)]$ in hexane at room temperature. Relevant crystallographic details are given in Table 2. A crystal was attached to a

Table 2
Crystal data and refinement details for **2**

Formula	$C_{14}H_{16}MoN_4O_4$
Formula weight	400.25
Temperature (K)	298(2)
λ (Mo–K_α) (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.873(1)
b (Å)	8.961(1)
c (Å)	13.043(1)
α (°)	92.891(1)
β (°)	90.279(1)
γ (°)	111.884(1)
V (Å^3)	852.5(1)
Z	2
D_{calc} (g cm^{-3})	1.559
Absorption coefficient (mm^{-1})	0.793
F(000)	404
Crystal size (mm); color	0.09 × 0.14 × 0.22; yellow
Index ranges	$-8 \leq h \leq 8$, $-9 \leq k \leq 9$, $-14 \leq l \leq 14$
Reflections collected	5584
Independent reflections	2444 [$R_{int} = 0.0201$]
Absorption correction	SADABS
Max/min transmission	1.0000 and 0.7668
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2444/0/221
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0230$, $wR_2 = 0.0607$
R indices (all data)	$R_1 = 0.0245$, $wR_2 = 0.0619$
Extinction coefficient	0.0086(11)
Largest difference peak and hole (e Å^{-3})	0.262 and −0.301

glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo–K_α X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to $2\theta = 46.54°$. Raw frame data were integrated with the SAINT program [20]. The structure was solved by direct methods with SHELXTL [21]. A semi-empirical absorption correction was applied with the program SADABS [22]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations and graphics were made with SHELXTL.

4. Supplementary material

CCDC-197054 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (internat.) +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk)].

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References

[1] (a) D. Braga, J. Chem. Soc. Dalton Trans. (2000) 3705.;
(b) G.R. Desiraju, J. Chem. Soc. Dalton Trans. (2000) 3745.

[2] C. Foces-Foces, A. Echevarría, N. Jagerovic, I. Alkorta, J. Elguero, U. Langer, O. Klein, M. Minguet-Bonvehí, H.-H. Limbach, J. Am. Chem. Soc. 123 (2001) 7898 (and references therein).

[3] Some examples of chains: (a) R. Graziani, U. Castellato, R. Ettore, G. Plazzogna, J. Chem. Soc. Dalton Trans. (1982) 805. (b) J.D. Crane, O.D. Fox, E. Sinn, J. Chem. Soc. Dalton Trans. (1999) 1461. (c) K. Sakai, Y. Tomita, T. Ue, K. Goshima, M. Ohminato, T. Tsubomura, K. Matsumoto, K. Ohmura, K. Kawakami, Inorg. Chim. Acta 64 (2000) 297. (d) A. Chadghan, J. Pons, A. Caubet, J. Casabó. J. Ros, A. Alvarez-Larena, J.F. Piniella, Polyhedron 19 (2000) 855.

[4] Some examples of dimers: (a) M.A. Cinellu, S. Stoccoro, G. Minghetti, A.L. Bandini, G. Banditelli, B. Bovio, J. Organomet. Chem. 372 (1989) 311. (b) M. Munakata, L.P. Wu, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, S. Kawata, S. Kitagawa, J. Chem. Soc. Dalton Trans. (1995) 4099. (c) G.A. Ardizzoia, G. La Monica, S. Cenini, M. Moret, N. Maschioni, J. Chem. Soc. Dalton Trans. (1996) 1351. (d) I.A. Guzei, C.H. Winter, Inorg. Chem. 36 (1997) 4415. (e) S.M. Couchman, J.C. Jeffery, M.D. Ward, Polyhedron (1999) 18, 2633.

[5] See for example: (a) L.A. Oro, D. Carmona, J. Reyes, C. Foces-Foces, F.H. Cano, J. Chem. Soc. Dalton Trans. (1986) 31. (b) D. Carmona, J. Ferrer, F.J. Lahoz, L.A. Oro, J. Reyes, M. Esteban, J. Chem. Soc. Dalton Trans. (1991) 2811. (c) G. López, J. Ruiz, C. Vicente, J.M. Martí, G. García, P.A. Chaloner, P.B. Hitchcock, R.M. Harrison, Organometallics 11 (1992) 4090. (d) D. Carmona, J. Ferrer, R. Atencio, F.J. Lahoz, L.A. Oro, M.P. Lamata, Organometallics 14 (1995) 2057. (e) G.A. Ardizzoia, G. La Monica, A. Maspero, N. Masciocchi, M. Moret, Eur. J. Inorg. Chem. (1999) 1301. (f) G.A. Ardizzoia, G. La Monica, A. Maspero, M. Moret, N. Masciocchi, Eur. J. Inorg. Chem. (2000) 181. (g) R. Contreras, M. Valderrama, E.M. Orellana, D. Boys, D. Carmona, L.A. Oro, M.P. Lamata, J. Ferrer, J. Organomet. Chem. 606 (2000) 197.

[6] P. Paredes, D. Miguel, F. Villafañe, Eur. J. Inorg. Chem., in press.

[7] A.D. Garnovskii, N.E. Kolobova, O.A. Osipov, K.N. Anisimov, I.B. Zlotina, G.K. Mitina, Y.V. Kolodyazhnyi, Zh. Obshch. Khim. 42 (1972) 929.

[8] (a) M.P. Gamasa, J. Gimeno, E. Lastra, S. García-Granda, D. Moreiras, J. Chem. Soc. Dalton Trans. (1991) 1557.;
(b) K.-B. Shiu, S.-T. Lin, C.-C. Chou, S.-M. Peng, M. -C. Cheng, S.-L. Wang, F.-L. Liao, J. Organomet. Chem. 469 (1994) 169;
(c) W.R. Thiel, T. Priermeier, D.A. Fiedler, A.M. Bond, M.R. Mattner, J. Organomet. Chem. 514 (1996) 137.

[9] (a) M. Millar, S. Lincoln, S.A. Koch, J. Am. Chem. Soc. 104 (1982) 288;
(b) H. Adams, N.A. Bailey, A.S. Drane, J.A. McCleverty, Polyhedron 2 (1983) 465;
(c) S.J. Rettig, A. Storr, J. Trotter, Can. J. Chem. 66 (1988) 97;
(d) F.A. Cotton, R.L. Luck, Acta Crystallogr. Sect. C 46 (1990) 138;
(e) P. Gili, P. Martín-Zarza, G. Martín-Reyes, J.M. Arrieta, G. Madariaga, Polyhedron 11 (1992) 115;
(f) M.K. Ehlert, S.J. Rettig, A. Storr, R.C. Thompson, J. Trotter, Inorg. Chem. 32 (1993) 5176;
(g) A. Wlodarczyk, S.S. Kurek, J.P. Maher, A.S. Batsanov, J.A.K. Howard, J.A. McCleverty, Polyhedron 12 (1993) 715;
(h) P. Martín-Zarza, P. Gili, F.V. Rodríguez-Romero, C. Ruiz-Pérez, X. Solans, Inorg. Chim. Acta 223 (1994) 173;
(i) M. Cano, J.A. Campo, J.V. Heras, E. Pinilla, A. Monge, Polyhedron 15 (1996) 1705;
(j) P. Gili, P.A. Lorenzo-Luis, A. Mederos, J.M. Arrieta, G. Germain, A. Castiñeiras, R. Carballo, Inorg. Chim. Acta 295 (1999) 106;
(k) A.M. Santos, F.E. Kühn, K. Bruus-Jensen, I. Lucas, C.C. Romão, E. Herdtweck, J. Chem. Soc. Dalton Trans. (2001) 1332.

[10] K. Bieger, G. Bouhadir, R. Reau, F. Dahan, G. Bertrand, J. Am. Chem. Soc. 118 (1996) 1038.

[11] W. Ries, I. Bernal, M. Quast, T.A. Albright, Inorg. Chim. Acta 83 (1984) 5.

[12] (a) G.A. Jeffrey, An Introduction to Hydrogen Bonding (Chapter 2), Oxford University Press, New York, 1997;
(b) T. Steiner, Angew. Chem. Int. Ed. Engl. 41 (2002) 48.

[13] D. Braga, F. Grepioni, Acc. Chem. Res. 30 (1997) 81.

[14] K. Heinze, J. Chem. Soc. Dalton Trans. (2002) 540.

[15] (a) D. Carmona, L.A. Oro, M.P. Lamata, J. Elguero, M.C. Apreda, C. Foces-Foces, F.H. Cano, Angew. Chem. Int. Ed. Engl. 25 (1986) 1114;
(b) D. Carmona, J. Ferrer, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, J. Elguero, M.L. Jimeno, J. Chem. Soc. Dalton Trans. (1990) 1463.;
(c) D. Röttger, G. Erker, M. Grehl, R. Fröhlich, Organometallics 13 (1994) 3897;
(d) D. Carmona, J. Ferrer, J.M. Arilla, J. Reyes, F.J. Lahoz, S. Elipe, F.J. Modrego, L.A. Oro, Organometallics 19 (2000) 798.

[16] R. Contreras, M. Valderrama, E.M. Orellana, D. Boys, D. Carmona, L.A. Oro, M.P. Lamata, J. Ferrer, J. Organomet. Chem. 606 (2000) 197.

[17] T. Beringhelli, G. D'Alonso, M. Panigati, F. Porta, P. Mercandelli, M. Moret, A. Sironi, Organometallics 17 (1998) 3282.

[18] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd ed, Pergamon Press, Oxford, 1988.
[19] R.B. King, Organomet. Synth. 1 (1965) 125.
[20] SAINT+. SAX area detector integration program. Version 6.02, Bruker AXS, Incorporation, Madison, WI, 1999.
[21] G.M. Sheldrick, SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data. Version 5.1, Bruker AXS, Incorporation, Madison, WI, 1998.
[22] G.M. Sheldrick, SADABS, Empirical Absorption Correction Program. University of Göttingen, Göttingen, Germany, 1997.