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The structural analysis of acetonitrile-*cis*-dicarbonyl(η^5-cyclopentadienyl)(triphenylphosphine)molybdenum(II) tetrafluoroborate, *cis*-$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)(NCCH_3)]^+[BF_4]^-$

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Abstract

The crystal structure of the title compound has been determined by means of single crystal X-ray diffraction techniques. The subject compound crystallizes in the monoclinic space group $P2_1/c$ (No. 14, C_{2h}^5). The lattice constants are $a=12.997(3)$, $b=11.729(3)$, $c=17.681(4)$ Å and $\beta=100.73(2)$°. Anisotropic refinement based on 3655 unique reflections using a full-matrix least-squares program has yielded $R=0.046$ and $R_w=0.051$. There are four molecules per unit cell, $D_m=1.52(3)$ and $D_x=1.52$ Mg m^{-3}. The tetrafluoroborate anion displayed a great deal of disorder. Utilizing cone angle calculations, a 'ligand profile' describes the steric bulk of the triphenylphosphine functional group. The resulting maximum cone angle, θ, for the triphenylphosphine group is 120°. Important metrical details are: Mo–P = 2.5356(8); Mo–N = 2.156(3); Mo–C = 1.978(4) and 1.950(4); C≡N = 1.120(4); and C≡O = 1.156(5) and 1.147(4) Å.

Introduction

The trisubstituted phosphine ligand (PR_3) has been shown to play a major role in facile metalation and hydrogen transfer reactions [1–3]. The steric bulk of these groups contributes to the rate of product formation and to the stereochemistry of the product. Often a configuration other than one that is electronically expected can result. This is due primarily to the very large or small size of the ligand in question. Faller and Anderson [4] studied *cis/trans* isomerism in $(\eta^5\text{-}C_5H_5)Mo(CO)_2LL'$ (where L = tertiary phosphine, L′ = anionic ligand) compounds as a function of the steric bulk of the L and L′ ligands. These authors found that the ratio of *cis* to *trans* isomers in solution ranged from less than 1:50 to greater than 50:1. It was also found that although both isomers may exist together in solution, only one isomer is present in the crystal phase.

Identification of isomers in solution has depended upon spectroscopic differences [4–8]. The *trans* isomers of $(\eta^5\text{-}C_5H_5)Mo(CO)_2LX$ compounds display a doublet C_5H_5 resonance in the ^1H NMR and a more intense lower frequency (antisymmetric) CO stretching vibration in the IR. The *cis* isomers display a singlet C_5H_5 resonance in the NMR and a more intense higher frequency (symmetric) CO stretch in the IR. Definitive isomer assignments can be made in the solid state by X-ray diffraction. A few such structures have been determined [8–10].

We have synthesized a number of complexes, including the title compound, by the oxidative cleavage of $[CpMo(CO)_2(PPh_3)]_2Hg$ [11], reported to exist in solution as the *trans* isomer [8]. The ^1H NMR and IR spectra of the title compound were consistent with it being formed exclusively as the *cis* isomer. Since it originated from a *trans* starting material and contained the rather bulky triphenylphosphine ligand, we were desirous of more firmly establishing its structure. The title compound readily formed single crystals on recrystallization from a number of solvents, so we proceeded to determine its crystal structure by X-ray diffraction.

This structural determination also allowed us to investigate the cone angle of the triphenylphosphine ligand. The concept of the cone angle, θ, as a measure of steric bulk for phosphine ligands was initiated by Tolman [12, 13]. This work was followed by the development of the rotational angle, ϕ, by Alyea *et al.* [14], Richardson and Payne [15], and Smith and Oliver [16]. A ligand profile (or silhouette profile) of the trisubstituted phosphine ligand yields a nu-

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merical value that represents the steric bulk of the ligand. This value may then be utilized to predict conformations and reaction rates and mechanisms.

Experimental

Red–orange diamond-shaped crystals with well defined edges of the title compound were synthesized as described elsewhere [11]. The quality of the data crystal was checked under a polarizing microscope. The selected crystal was mounted on a glass fiber and transferred to an Enraf-Nonius CAD-4F auto-diffractometer equipped with a dense graphite incident-beam monochromator, take-off angle 5.8°. Twenty-five randomly selected and well-centered reflections were used to determine the unit cell parameters (see Table 1) and the orientation matrix. Systematic absences ($h0l$, $l=2n+1$, and $0k0$, $k=2n+1$) revealed the appropriate space group assignment, $P2_1/c$ (No. 14, C_{2h}^5). Intensity data were obtained using the ω–2θ scan technique with a variable scan rate (0.39 to 3.35° min^{-1}) determined by a fast prescan of 3.35° min^{-1}. Data were collected using Mo K$\bar{\alpha}$ radiation ($\lambda_{mean}=0.71073$ Å) in the range of $3.0<2\theta<45.0°$ at a variable scan width of $1.25+0.35 \tan \theta$. Three standard reflections ($\bar{1}\bar{1}5$, $\bar{1}08$, and 444) were monitored every two hours of data collection time and revealed no substantial variation in intensity (<0.3%) which verified crystal stability and instrument reliability. Lorentz and polarization corrections were applied to the data as well as an absorption correction ($\mu = 5.9$ cm^{-1}) based on the crystal shape and dimensions. The numerical absorption correction [17] was based upon Gaussian integration methods expressed by Coppens *et al.* [18]. After averaging redundant data ($R_{int}=0.025$), 3655 reflections were greater than $3\sigma(I)$. Table 1 presents a summary of experimental conditions and statistical data.

The phase problem was solved employing MULTAN [17], which yielded the molybdenum and several other atomic positions. All other atomic positions were located through the use of DIRDIF [17] and through a series of electron density difference Fourier maps. Several isotropic refinement cycles using a full-matrix least-squares program [17] settled the heavy metal, phosphorous, oxygen, nitrogen, and carbon atomic positions and their thermal motion. This was necessary before attempting the refinement of the BF_4^- anion which displayed a high degree of disorder regarding the fluorine atoms. Thirteen different fluorine positions, constituting a total occupancy of four fluorine atoms, were obtained through difference Fourier mapping. The fluorine thermal parameters were always held constant, $B_{iso}=5.0$. However, the multiplicities for the fluorine atoms were refined. This procedure was used by Allen *et al.* [19] in the refinement of the BF_4^- in a similar compound, $[Mo\{\eta^4\text{-}C(CH_2)_3\}(CO)_2(\eta^5\text{-}C_5Me_5)]^+[BF_4]^-$. Then, after several cycles of anisotropic refinement, the R factors stabilized with a maximum shift/error value of 8.0×10^{-2}. The shift/error value is defined as $[\Delta\xi_i/\sigma(\xi_i)]$ where ξ_i values are varied parameters. A correction for extinction (g) [20] was also made (see Table 1) and hydrogen atom positions were idealized (at C–H = 1.07 Å) and not refined. The residual and weighted indices used in the structural refinement are $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.046$ and $R_w=(\Sigma w||F_o|-|F_c||^2/\Sigma w|F_o|^2)^{1/2}=0.051$ where $w=\sigma^{-2}(|F_o|)$. The minimized quantity was $\Sigma w||F_o|-|F_c||^2$. The largest peak of residual density remaining after the final anisotropic refinement cycle was 0.8 e$^-$ Å^{-3} (minimum, −0.6 e$^-$ Å^{-3}) in the vicinity of the heavy metal. Elsewhere, the final electron density map was virtually featureless. Atomic scattering factors and associated anomalous dispersion factors were taken from the International Tables [21]. Atomic coordinates and equivalent isotropic thermal parameters with estimated standard deviations are listed in Table 2. Positions for the idealized hydrogen atoms are listed in Table 3. See also 'Supplementary material'.

TABLE 1. Experimental and statistical summaries for *cis*-$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)(NCCH_3)]^+[BF_4]^-$

Empirical formula	$MoPNO_2C_{27}H_{23}BF_4$
Space group	$P2_1/c$ (No. 14, C_{2h}^5)
M_r	607.21
Radiation (Mo K$\bar{\alpha}$, Å)	0.71073
a (Å)	12.997(3)
b (Å)	11.729(3)
c (Å)	17.681(4)
β (°)	100.73(2)
V (Å^3)	2648.20
D_m (Mg m^{-3})	1.52(3)
D_x (Mg m^{-3})	1.52
Z	4
$F(000)$ (e$^-$)	1224
μ (Mo K$\bar{\alpha}$) (cm^{-1})	5.9
$\Delta\theta$ (°)	1.5–22.5
R_{int}	0.025
R	0.046
R_w	0.051
Unique reflections (>3σ)	3655
g (e^{-2}) ($\times10^{-8}$)	9.18
Shift/error $[\Delta\xi_i/\sigma(\xi_i)]$ ($\times10^{-2}$)	
maximum	8.0
average	1.5
Residual density (e$^-$ Å^{-3})	
maximum	0.795
minimum	−0.601

TABLE 2. Atomic positions and equivalent isotropic thermal parameters for *cis*-$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)(NCCH_3)]^+[BF_4]^-$

Atom	*x*	*y*	*z*	Occupancy	U_{eq} [a]
Mo	0.73957(3)	0.89887(3)	0.58469(2)	1	2.375(9)
P	0.73847(9)	0.7599(1)	0.47472(7)	1	2.46(2)
O(1)	0.6370(4)	0.8895(4)	0.7315(3)	1	6.8(1)
O(2)	0.5019(3)	0.8741(4)	0.5214(3)	1	5.0(1)
N	0.8211(3)	0.7545(3)	0.6431(2)	1	3.06(9)
C(1)	0.6756(5)	0.8903(5)	0.6777(3)	1	4.1(1)
C(2)	0.5903(4)	0.8824(4)	0.5438(3)	1	3.3(1)
C(3)	0.8620(4)	0.6778(5)	0.6722(3)	1	3.7(1)
C(4)	0.9128(6)	0.5758(5)	0.7102(5)	1	7.0(2)
C(11)	0.8498(4)	1.0101(4)	0.5209(3)	1	3.6(1)
C(12)	0.7501(4)	1.0648(4)	0.5178(3)	1	3.6(1)
C(13)	0.7385(4)	1.0912(4)	0.5930(3)	1	3.8(1)
C(14)	0.8287(4)	1.0548(5)	0.6441(3)	1	4.2(1)
C(15)	0.8983(4)	1.0028(5)	0.5998(3)	1	4.0(1)
C(21)	0.6493(4)	0.8041(4)	0.3873(3)	1	2.9(1)
C(22)	0.6771(5)	0.9000(5)	0.3470(3)	1	4.0(1)
C(23)	0.6059(5)	0.9405(6)	0.2829(4)	1	5.4(2)
C(24)	0.5112(5)	0.8855(6)	0.2599(4)	1	5.5(2)
C(25)	0.4849(4)	0.7905(6)	0.2997(3)	1	4.9(1)
C(26)	0.5540(4)	0.7504(5)	0.3631(3)	1	3.8(1)
C(31)	0.8633(4)	0.7379(4)	0.4448(3)	1	2.8(1)
C(32)	0.9558(4)	0.7384(5)	0.4999(3)	1	3.7(1)
C(33)	1.0518(4)	0.7134(5)	0.4803(4)	1	4.3(1)
C(34)	1.0571(4)	0.6888(5)	0.4032(3)	1	4.1(1)
C(35)	0.9677(4)	0.6878(5)	0.3486(3)	1	4.2(1)
C(36)	0.8714(4)	0.7131(5)	0.3691(3)	1	3.8(1)
C(41)	0.6974(4)	0.6135(4)	0.4927(3)	1	2.9(1)
C(42)	0.6476(4)	0.5918(4)	0.5541(3)	1	3.4(1)
C(43)	0.6184(5)	0.4799(5)	0.5682(3)	1	4.6(1)
C(44)	0.6370(5)	0.3916(5)	0.5189(4)	1	4.4(1)
C(45)	0.6828(5)	0.4139(5)	0.4577(4)	1	4.5(1)
C(46)	0.7163(4)	0.5258(5)	0.4440(3)	1	3.9(1)
B	0.1775(5)	0.7028(6)	0.1974(4)	1	4.4(2)
F(1)	0.262(2)	0.703(3)	0.158(2)	0.440	5.0[b]
F(2)	0.222(4)	0.672(5)	0.145(3)	0.261	5.0[b]
F(3)	0.133(3)	0.609(3)	0.158(2)	0.402	5.0[b]
F(4)	0.085(3)	0.652(4)	0.181(2)	0.351	5.0[b]
F(5)	0.220(2)	0.677(2)	0.269(1)	0.650	5.0[b]
F(6)	0.101(3)	0.774(4)	0.189(2)	0.326	5.0[b]
F(7)	0.855(2)	0.324(3)	0.325(2)	0.455	5.0[b]
F(8)	0.205(3)	0.834(3)	0.204(2)	0.371	5.0[b]
F(9)	0.737(5)	0.243(5)	0.229(3)	0.228	5.0[b]
F(10)	0.210(9)	0.77(1)	0.174(7)	0.117	5.0[b]
F(11)	0.072(6)	0.706(7)	0.202(4)	0.181	5.0[b]
F(12)	0.228(9)	0.63(1)	0.264(7)	0.114	5.0[b]
F(13)	0.19(1)	0.66(1)	0.144(8)	0.105	5.0[b]

[a] Equivalent isotropic thermal parameter (U_{eq}) defined as 1/3 the trace of the orthogonalized U_{ij} tensor. [b] The atomic positions and occupancies were refined. The thermal parameters were held constant ($B_{iso}=5.0$).

Results and discussion

The central molybdenum atom is considered to be seven-coordinated due to the fact that the η^5-cyclopentadienyl ring is formally a tridentate ligand. A more logical point of view is that the molybdenum atom is pseudo five-coordinated. The arrangement of the functional groups about the molybdenum atom is that of a distorted square pyramid with the η^5-cyclopentadienyl ring at the apex of the pyramid, see Fig. 1. This 'four-legged piano stool' configuration [22] serves as a model for these types of complexes.

In the slightly distorted square-pyramidal arrangement, the four legs of the piano stool are comprised of two carbonyl groups, an acetonitrile group and a triphenylphosphine group, see Figs. 1 and 2. In

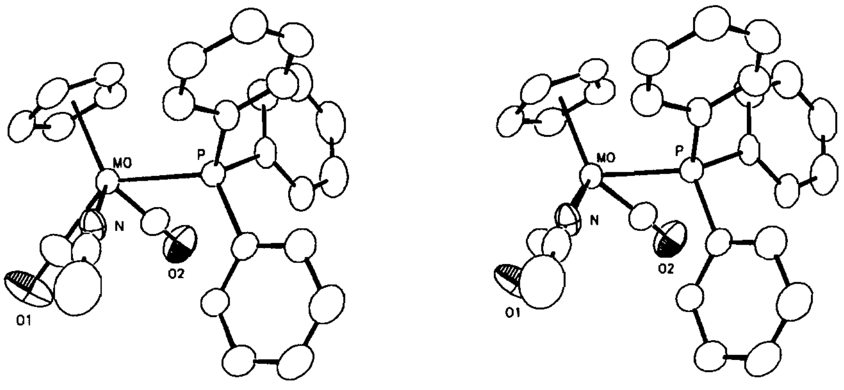

Fig. 1. A stereo view of the *cis*-[(η^5-C_5H_5)Mo(CO)$_2$(PPh$_3$)(NCCH$_3$)]$^+$ cation showing the 'four-legged piano stool' conformation of the ligands surrounding the molybdenum atom.

TABLE 3. Hydrogen atom positions[a] for the *cis*-[(η^5-C_5H_5)Mo(CO)$_2$(PPh$_3$)CH$_3$CN]$^+$ cation

Atom	x	y	z
H(11)	0.8818	0.9802	0.4723
H(12)	0.6935	1.0824	0.4661
H(13)	0.6715	1.1325	0.6091
H(14)	0.8432	1.0643	0.7059
H(15)	0.9735	0.9650	0.6223
H(21)	0.7518	0.9414	0.3652
H(22)	0.6251	1.0142	0.2517
H(23)	0.4568	0.9166	0.2104
H(24)	0.4106	0.7482	0.2810
H(25)	0.5335	0.6768	0.3939
H(31)	0.9524	0.7587	0.5589
H(32)	1.1220	0.7128	0.5239
H(33)	1.1316	0.6707	0.3872
H(34)	0.9714	0.6674	0.2895
H(35)	0.8015	0.7135	0.3250
H(41)	0.6314	0.6605	0.5907
H(42)	0.5816	0.4616	0.6168
H(43)	0.6145	0.3053	0.5298
H(44)	0.6940	0.3457	0.4189
H(45)	0.7557	0.5427	0.3965

[a]Hydrogen atom positions were idealized according to C–H = 1.07 Å and were not refined.

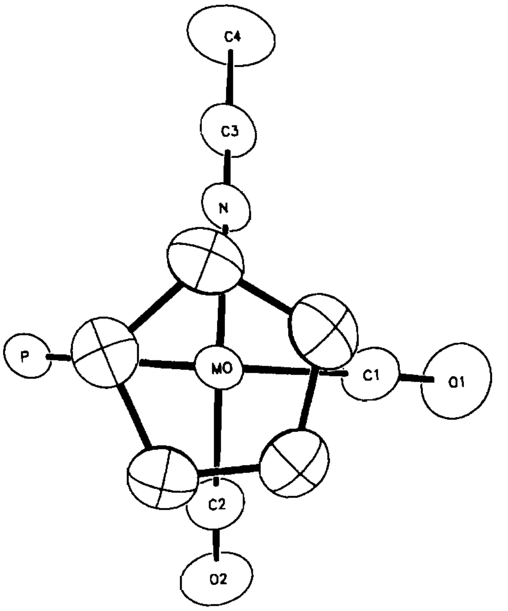

Fig. 2. Drawing of the *cis*-[(η^5-C_5H_5)Mo(CO)$_2$-(PPh$_3$)(NCCH$_3$)]$^+$ cation looking down the centroid of the cyclopentadienyl plane. The three phenyl rings bonded to the phosphorous atom have been omitted for clarity.

agreement with solution spectroscopic data, the two carbonyl groups are *cis* to one another. The involved bond angles are: C(1)–Mo–N = 78.9(1); C(1)–Mo–C(2) = 76.1(2); C(2)–Mo–P = 77.8(1); and N–Mo–P = 78.15(7)°. The average Mo–C(O) bond length of 1.964(14) Å (see Table 4) is in good agreement with the experimental average M–C(O) bond length, 1.970(18) Å, observed in the structural analysis of a similar complex [(η^5-C_5H_5)Mo(CO)$_3$HgCl] by Bueno and Churchill [23] and with the 1.97 Å bond distance used in the extended-Hückel-molecular-orbital (EHMO) calculations found in the work of Allen *et al.* [19], as well as being in accord with established bond distances found in BIDICS [24]. There appears to be strong directional bonding related to the interaction of the molybdenum 4d orbitals with the CO orbitals, which is confirmed by the Mo—C≡O bond angles of 177.4(3) and 178.2(3)°, see Table 5. The average C≡O bond length of 1.152(4) Å is also in accord with refs. 23 (1.146(10) Å) and 24. The acetonitrile group (N≡C—CH$_3$) forms an almost straight chain with the center Mo atom. The involved bond angles are 178.3(3)° for Mo—N≡C and 178.5(4)° for N≡C—C. The respective Mo–N and C≡N bond distances of 2.156(3) and 1.120(4) Å are also in agreement with published experimental values [24].

TABLE 4. Selected bond lengths (Å) for *cis*-$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)(NCCH_3)]^+[BF_4]^-$

Atom 1	Atom 2	Length	Atom 1	Atom 2	Length
Mo	P	2.5356(8)	P	C(21)	1.826(3)
Mo	N	2.156(3)	P	C(31)	1.816(3)
			P	C(41)	1.842(3)
Mo	C(1)	1.978(4)	Av.		1.828(11)
Mo	C(2)	1.950(4)			
Av.		1.964(14)	B	F(1)	1.41(1)
			B	F(2)	1.24(2)
C(1)	O(1)	1.156(5)	B	F(3)	1.38(1)
C(2)	O(2)	1.147(4)	B	F(4)	1.32(1)
Av.		1.152(4)	B	F(5)	1.32(1)
			B	F(6)	1.28(1)
C(3)	N	1.120(4)	B	F(7)	1.51(1)
C(3)	C(4)	1.468(5)	B	F(8)	1.58(1)
			B	F(9)	1.61(2)
Mo	C(11)	2.375(3)	B	F(10)	1.05(4)
Mo	C(12)	2.299(3)	B	F(11)	1.39(3)
Mo	C(13)	2.259(3)	B	F(12)	1.51(5)
Mo	C(14)	2.311(3)	B	F(13)	1.13(5)
Mo	C(15)	2.369(3)	Av.		1.36(14)
Av.		2.32(5)			
Mo···centroid		1.971			

TABLE 5. Selected angles (°) for *cis*-$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)(NCCH_3)]^+[BF_4]^-$

Atom 1	Atom 2	Atom 3	Angle
C(1)	Mo	N	78.9(1)
C(1)	Mo	C(2)	76.1(2)
C(2)	Mo	P	77.8(1)
P	Mo	N	78.15(7)
C(1)	Mo	P	131.4(1)
C(2)	Mo	N	117.8(1)
Mo	N	C(3)	178.3(3)
N	C(3)	C(4)	178.5(4)
Mo	C(1)	O(1)	177.4(3)
Mo	C(2)	O(2)	178.2(3)
C(21)	P	C(31)	104.8(1)
C(21)	P	C(41)	104.6(1)
C(31)	P	C(41)	102.8(1)
Mo	P	C(21)	112.2(1)
Mo	P	C(31)	115.9(1)
Mo	P	C(41)	115.3(1)
Av.			109.3
Mo	P	C(26)	116.50(8)
Mo	P	C(36)	135.66(8)
Mo	P	C(46)	139.84(8)
P	C(21)	C(22)	118.1(2)
P	C(31)	C(32)	119.7(2)
P	C(41)	C(42)	119.9(2)
P	C(21)	C(26)	121.5(2)
P	C(31)	C(36)	122.7(2)
P	C(41)	C(46)	119.4(3)
Av.			120.2

The Mo–P distance, 2.5356(8) Å, and the average P–C distance of 1.828(11) Å are in line with results, 2.481(5) and 1.826(17) Å, respectively, observed in a related structure, $(\eta^5\text{-}CH_5)Mo(CO)_2(PPh_3)I$, by Bush *et al.* [25]. The C–P–C bond angles are considerably less (mean, 104.1(9)°) than the expected ideal tetrahedral angle of 109.5° while the average Mo–P–C bond angle is considerably larger, 114.5(16)°.

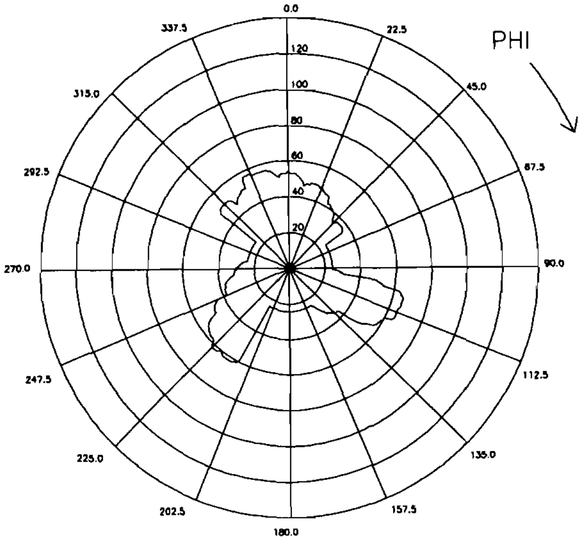

Fig. 3. The ligand profile ($\theta/2$ vs. ϕ) of the PPh_3 functional group in the *cis*-$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)(NCCH_3)]^+$ cation.

TABLE 6. Bond lengths (Å) and angles (°) for atoms in rings in the *cis*-[(η^5-C_5H_5)Mo(CO)$_2$(PPh$_3$)(NCCH$_3$)]$^+$ cation

Atom 1	Atom 2	Length	Atom 1	Atom 2	Atom 3	Angle
C(11)	C(12)	1.438(5)	C(11)	C(12)	C(13)	108.5(3)
C(12)	C(13)	1.401(5)	C(12)	C(13)	C(14)	108.6(3)
C(13)	C(14)	1.406(5)	C(13)	C(14)	C(15)	108.2(3)
C(14)	C(15)	1.438(5)	C(14)	C(15)	C(11)	107.5(3)
C(11)	C(15)	1.423(5)	C(15)	C(11)	C(12)	107.2(3)
	mean	1.421(16)			mean	108.0(6)
C(21)	C(22)	1.414(5)	C(21)	C(22)	C(23)	118.9(4)
C(22)	C(23)	1.406(5)	C(22)	C(23)	C(24)	119.7(4)
C(23)	C(24)	1.382(7)	C(23)	C(24)	C(25)	120.9(4)
C(24)	C(25)	1.395(6)	C(24)	C(25)	C(26)	119.8(4)
C(25)	C(26)	1.381(5)	C(21)	C(26)	C(25)	120.4(4)
C(26)	C(21)	1.385(4)	C(22)	C(21)	C(26)	120.3(3)
	mean	1.394(12)			mean	120.0(6)
C(31)	C(32)	1.400(4)	C(31)	C(32)	C(33)	121.4(3)
C(32)	C(33)	1.386(5)	C(32)	C(33)	C(34)	119.6(3)
C(33)	C(34)	1.409(5)	C(33)	C(34)	C(35)	119.9(3)
C(34)	C(35)	1.365(5)	C(34)	C(35)	C(36)	120.0(3)
C(35)	C(36)	1.399(5)	C(31)	C(36)	C(35)	119.9(3)
C(36)	C(31)	1.393(5)	C(32)	C(31)	C(36)	117.5(3)
	mean	1.392(14)			mean	119.7(11)
C(41)	C(42)	1.388(5)	C(41)	C(42)	C(43)	119.5(3)
C(42)	C(43)	1.401(5)	C(42)	C(43)	C(44)	119.8(4)
C(43)	C(44)	1.403(5)	C(43)	C(44)	C(45)	120.4(3)
C(44)	C(45)	1.355(6)	C(44)	C(45)	C(46)	120.7(3)
C(45)	C(46)	1.418(5)	C(41)	C(46)	C(45)	118.9(3)
C(46)	C(41)	1.393(5)	C(42)	C(41)	C(46)	120.6(3)
	mean	1.393(19)			mean	120.0(6)

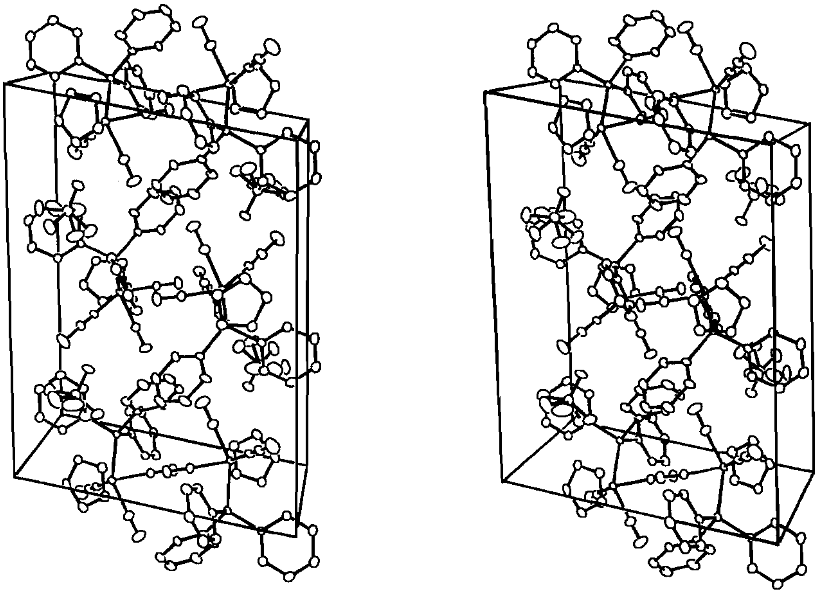

Fig. 4. The molecular packing diagram of *cis*-[(η^5-C_5H_5)Mo(CO)$_2$(PPh$_3$)(NCCH$_3$)]$^+$[BF$_4$]$^-$.

This difference from ideality could be due to steric repulsion caused by the bulkiness of the other functional groups associated with the Mo atom. The planarity of each phenyl ring was confirmed using the program PLANES [17]. The deviations from planarity for the three rings were 0.003, 0.004, and 0.010 Å. Individual bond lengths and angles are listed in Table 6. The mean bond distances in each phenyl ring can be considered ideal [26, 27]. The orientation of the three phenyl rings can be represented in terms of a cone angle [12–16]. The computer program CONE [16] was used to present the ligand profile, see Fig. 3. This ligand profile is the silhouette of the triphenylphosphine functional group obtained by looking down the molybdenum–phosphorus bond. The outlines of the phenyl rings are clearly seen. The maximum half cone angle, $\theta/2_{\max}$, for the triphenylphosphine group in this compound is approximately 60°, making $\theta \approx 120°$. Figure 4 gives a stereoview of the orientation of the phenyl rings and the molecular packing.

The least-squares planes program [17] also verified the planarity of the η^5-C_5H_5 ring, deviation <0.004 Å. The η^5-C_5H_5 ligand is the seat of the 'four-legged piano stool', located at the apex of the pyramidal base consisting of the four monodentate ligands. The molybdenum–carbon (η^5-C_5H_5) bond lengths range from 2.259(3) to 2.375(3) Å, yielding a mean Mo–C(ring) distance of 2.32(6) Å and a Mo···centroid (located at 0.814, 1.042, 0.572) contact distance of 1.971 Å, all of which are in agreement with the work of Allen *et al.* [19] and Bueno and Churchill [23]. The mean C–C bond length in the five-membered ring is 1.421(16) Å and the average C–C–C bond angle is 108.0(6)°, see Table 5. Finally, the tetrafluoroborate shows a great deal of disorder, which is quite common for this anion. Thirteen distinct fluorine positions were located. The populations of these positions range from 0.105 to 0.650, but the sum constitutes a total occupancy of four fluorine atoms. Although the orientation of the boron atom within the unit cell is established, the orientation of the fluorine atoms in the anion varies from unit cell to unit cell. The B–F bond lengths vary considerably. Nevertheless, the average B–F distance of 1.36(16) Å is in direct agreement with the experimental average B–F distance of 1.40(5) Å observed in the crystal structural analysis of $[\mathrm{Mo}\{\eta^4\text{-}\mathrm{C(CH_2)_3}\}\mathrm{(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})]^+[\mathrm{BF_4}]^-$ by Allen *et al.* [19]. Even though many of the bond angles in the anion were close to 109.5°, no perfect or distorted tetrahedra could factually be observed. The anion location with reference to the cation species is clearly seen in the stereoscopic view of the molecular packing of the unit cell. A total of four complete molecules are located within the monoclinic unit cell, with the individual molecules arranged head to tail about a 2_1 screw axis. The packing arrangement also emphasizes the glide plane within the unit cell.

Conclusions

Complexes of the type $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{M(CO)_2LL'}$ (where M = Mo or W, L = tertiary phosphine, L′ = anionic or neutral ligand) have an extensive chemistry. One aspect of this chemistry is the existence of *cis* and *trans* isomers, the predominant isomer being determined by both steric and electronic considerations. Identification of the isomer or isomers present in solution has most commonly depended on NMR and IR spectroscopic differences. We have shown that these assignments are most likely reliable since in our case the NMR and IR spectra and the X-ray crystal structure agree. We have also provided further data about the bulk, as expressed in the cone angle, of the widely encountered triphenylphosphine ligand.

Supplementary material

Structure factor tables and anisotropic thermal parameters are available from author D.F.M.

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