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Strong Interaction between an Aliphatic Carbon–Hydrogen Bond and a Metal Atom: The Structure of (Diethylbis(1-pyrazolyl)borato)allyldicarbonylmolybdenum(II)

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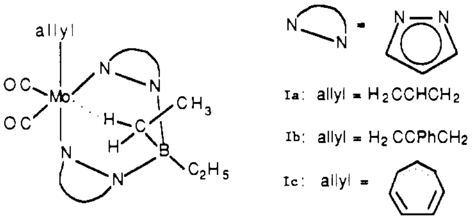
The structure of (diethylbis(1-pyrazolyl)borato)allyldicarbonylmolybdenum(II) is reported, as determined in a single-crystal X-ray structure study. This complex contains a very short Mo to H distance (2.11–2.24 Å), which suggests a strong interaction between an aliphatic carbon–hydrogen bond and the molybdenum atom. This complex and some other closely related analogues were the first complexes known to exhibit this phenomenon. Crystal data: $[Et_2B(Pz)_2](CO)_2(\eta^3\text{-}H_2CCHCH_2)Mo$, triclinic, space group $P\bar{1}$, $a = 6.8541$ (9) Å, $b = 8.028$ (1) Å, $c = 17.398$ (3) Å, $\alpha = 97.64$ (1)°, $\beta = 90.62$ (1)°, $\gamma = 109.33$ (1)°, $V = 893.3$ (2) Å^3, $Z = 2$, $R = 0.029$ ($R_w = 0.041$) for 292 parameters and 3871 unique data having $F_o > 3\sigma(F_o^2)$. The question of what is meant by the position of a hydrogen atom in this type of situation is also discussed, and the equal validity of neutron and X-ray results is asserted.

Introduction

The ability of C–H bonds to interact strongly with nearby metal atoms in certain organometallic compounds is now generally recognized as an important factor in the organometallic chemistry of the transition metals. It was first recognized, extensively explored, and thoroughly explained in a series of papers[1–3] published from this laboratory in 1974. The compounds studied were those shown as Ia–c.



The stimulus for this work can be found in two earlier papers[4,5] describing complexes similar to Ic, but with the important difference that instead of the diethylbis(1-pyrazolyl)borate ligand $(C_2H_5)_2B(Pz)_2$ (Pz = 1-pyrazolyl) with its $B(C_2H_5)_2$ group they had a $H_2B(Pz')_2$ (Pz′ = 3,5-Me_2Pz) ligand. It was found by X-ray studies of these compounds that the dihydrobis(3,5-dimethyl-1-pyrazolyl)borate chelate ring has a pronounced boat conformation "with one of the hydrogen atoms on the boron atom approaching the molybdenum atom closely, forming a B–H–Mo three-center, two-electron bond" and that the molybdenum atom, therefore, "need not be considered to have a 16-electron configuration".

From this observation came the idea that in a complex of type I, especially Ia and Ib, the metal atom might achieve an 18-electron configuration by way of a three-center, two-electron C–H–Mo bond. As explicitly stated,[1] "it was with the hope, and expectation, that an unprecedentedly strong aliphatic C–H to metal interaction could be examined" that the study of compounds of type I was undertaken. It was further noted[1] to be "only a short extrapolation from the situation just discussed (i.e., that in the $H_2B(Pz')_2$ compounds) to consider that a C–H···Mo interaction might be found" if "the H_2B is replaced by R_2B, with R being some aliphatic group".

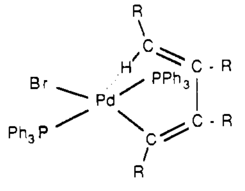
The purpose of the foregoing review is to make it clear that the discovery of strong C–H···M interactions, which occur in order to allow metal atoms that would otherwise be lacking electrons to achieve a preferred population, was no accident but rather the result of a rational and deliberate plan.

Our initial desire was to examine compound Ia, but since Ib was strongly represented to us by Trofimenko[6] as more tractable (and he also kindly supplied a sample of Ib), the X-ray crystal structure of this compound was determined.[1] The result completely confirmed the expectation. The structure was "such as to direct one of the α-hydrogen atoms toward the molybdenum atom. The H···Mo distance appears to be not more than 2.27 (8) Å and possibly as short as about 2.15 Å. A three-center, two-electron bond encompassing the C···H···Mo atoms is postulated to account for this strong interaction and to provide the molybdenum atom with an effective closed-shell configuration". The uncertainty about the exact value of the extremely short Mo···H distance was due to the fact that the structure was determined by X-ray crystallography. Persistent efforts to grow crystals large enough to obtain neutron diffraction data were unsuccessful. However, as we shall show later, there is a serious problem as to what the results of either type of structure determination actually mean.

Nevertheless, the concept of a strong C–H···M interaction was shown here (for the first time) to be a reality, and the general importance of such interactions (e.g., in catalysis) was explicitly emphasized, both in this paper and in a second one that followed shortly.[2] In this second paper, an NMR study of the dynamic behavior of Ia and Ib was reported and it was pointed out that a fluxional molecule of this type "constitutes a model for the interaction of a saturated hydrocarbon with a hypovalent metal atom, a process which must be involved in the initial stage of any catalytic process that involves activation of saturated hydrocarbons for reaction or rearrangement". Moreover, from the NMR results it was estimated that the strength of the C–H···Mo interaction is 17–20 kcal mol^{-1}.

Finally, in a structural study[3] of Ic the interesting and important point that "a C–H–Mo interaction...is structurally and thermodynamically competitive with olefin-metal bonding" was established. In this compound, it was inferred from the C···Mo distance that the H···Mo distance is about 0.20 Å shorter than that in Ib (i.e., ca. 1.93 Å).

In connection with the statement above that the 1974 report on Ib represented the *first time* that the concept of a *strong C–H···M interaction* was shown to be a reality, it is necessary to comment on the compound II, which was reported in 1972.[7] The



II: R = CO_2Me

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[6] (a) Trofimenko, S. *J. Am. Chem. Soc.* **1968**, *90*, 4754; (b) *Inorg. Chem.* **1970**, *9*, 2493.

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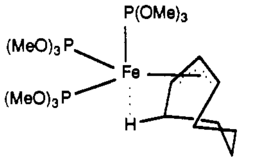
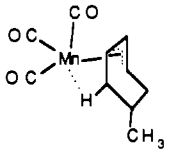
interaction here does not represent donation of C–H electron density to a metal atom that would otherwise have less than its normal number of electrons. The square *trans*-PdBr(CRCRCRCRH)$(PPh_3)_2$ unit prior to any H···Pd approach is already a conventional, square, 16-electron complex, of which there are thousands of examples that are entirely stable, and furthermore, this interaction does not require any distortions of the butadienyl group that would create steric strain in the molecule. This is quite different from the case of a 16-electron Mo compound, which would have a *strong* tendency to obtain a share in an additional pair of electrons, even at the cost of strain and distortion.

Some 5–10 years after the work in ref 1–3 was published, some iron[8] and manganese[9] compounds, III and IV, were reported in which the hydrogen atoms were actually located in neutron diffraction studies. The M···H distances were on the order of 1.85 Å for these first-row transition-metal atoms. This is entirely consistent with the fact that these atoms are ca 0.1 Å smaller than the Mo atom[10] and that the H atoms are clearly constrained by the ligand structures to lie close to the metal atoms. Examples of C–H···M interactions (for which the curious word "agostic" has been suggested) that are not in any essential way different from those originally described in 1974 have continued to multiply.[11] It is satisfying to see how seminal, and how conceptually right, the original work was, even though it was well ahead of its time. Unfortunately, this work is often ignored by some who mistakenly equate the invention of the term "agostic" with the actual *discovery* of the phenomenon it is supposed to describe.



III



IV

In this laboratory we have redirected attention to compounds of type I by preparing and crystallizing Ia. We found that it could be grown as crystals large enough for neutron diffraction study, but regrettably, these crystals cannot be cooled (to ca. 80 K) for neutron study without cracking. While this is disappointing, it was gratifying to find that at ambient temperature crystals of Ia diffract X-rays *extremely* well and it has been possible to obtain an exceptionally precise and informative X-ray structure, including *refined* positions for *all* hydrogen atoms.

Experimental Section

The complex $[Et_2B(Pz)_2](CO)_2(\eta^3\text{-}H_2CCHCH_2)Mo$ (Ia) was prepared according to the published procedure.[6b] Crystals suitable for X-ray diffraction were obtained by allowing slow crystallization out of a concentrated solution of Ia in hexane. One crystal was selected, coated with epoxy resin, and mounted on top of a glass fiber. Some relevant crystallographic information is given in Table I. The X-ray data were collected and corrected as previously described.[12] Most of the positions of the non-hydrogen atoms could be discerned from a three-dimensional Patterson function. The rest were located in a series of least-squares full-matrix isotropic refinements and difference maps. This model, consisting of all of the non-hydrogen atoms, was then refined anisotropically to convergence. A difference map at this stage revealed peaks indicative of most of the hydrogen atoms in the structure, including the one involved in the C–H···M interaction (see Figure 1, atom H(71)). These were all entered as hydrogen atoms and refined without constraints to convergence. The positions of all the remaining hydrogen atoms were then located in a difference map, and this complete model was refined to convergence, resulting in the final figures of merit listed in Table I. The fractional atomic coordinates and bond distances and angles are given in Tables II and III, respectively.

Table I. Crystallographic Data for $[Et_2B(Pz)_2](CO)_2(\eta^3\text{-}H_2CCHCH_2)Mo$ (Ia)

$C_{15}H_{21}BN_4O_2Mo$	fw: 396.11
$a = 6.8541$ (9) Å	space group: $P\bar{1}$ (No. 2)
$b = 8.028$ (1) Å	$T = 19$ °C
$c = 17.398$ (3) Å	$\lambda = 0.71073$ Å
$\alpha = 97.64$ (1)°	$\rho_{obsd} = 1.472$ g cm^{-3}
$\beta = 90.62$ (1)°	$\mu = 7.274$ cm^{-1}
$\gamma = 109.33$ (1)°	transmissn coeff: 99.91–87.12
$V = 893.8$ (2) Å^3	$R(F_o)^a = 0.028$
$Z = 2$	$R_w(F_o)^b = 0.041$

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table II. Positional Parameters and Their Estimated Standard Deviations for $[Et_2B(pz)_2](CO)_2(\eta^3\text{-}H_2CCHCH_2)Mo$ (Ia)[a]

atom	x	y	z	B, Å^2
Mo	0.09432 (2)	0.27596 (2)	0.33884 (1)	2.507 (3)
O(11)	0.3368 (3)	0.2996 (3)	0.4928 (1)	5.98 (5)
O(12)	0.0848 (4)	0.6371 (2)	0.4260 (1)	6.67 (5)
N(1)	0.3560 (2)	0.4363 (2)	0.28062 (8)	2.64 (3)
N(2)	0.3712 (2)	0.3916 (2)	0.20336 (9)	2.56 (3)
N(3)	0.1755 (2)	0.0585 (2)	0.2667 (1)	2.87 (3)
N(4)	0.1919 (2)	0.0633 (2)	0.1888 (1)	2.91 (3)
C(1)	0.5555 (3)	0.4934 (3)	0.1828 (1)	3.26 (4)
C(2)	0.6626 (3)	0.6084 (3)	0.2474 (1)	3.69 (4)
C(3)	0.5324 (3)	0.5678 (2)	0.3075 (1)	3.36 (4)
C(4)	0.2354 (3)	−0.0811 (3)	0.1559 (1)	3.89 (4)
C(5)	0.2502 (3)	−0.1818 (2)	0.2134 (2)	4.49 (5)
C(6)	0.2144 (3)	−0.0884 (2)	0.2819 (1)	3.78 (4)
C(7)	−0.0294 (3)	0.2701 (2)	0.1751 (1)	3.06 (3)
C(8)	−0.2229 (3)	0.1194 (4)	0.1386 (2)	4.97 (6)
C(9)	0.2273 (3)	0.2173 (3)	0.0639 (1)	4.11 (5)
C(10)	0.1979 (5)	0.3634 (5)	0.0212 (2)	6.47 (7)
C(11)	0.2464 (3)	0.2881 (3)	0.4351 (1)	3.72 (4)
C(12)	0.0827 (4)	0.5031 (3)	0.3928 (1)	4.15 (4)
C(13)	−0.2466 (3)	0.2497 (3)	0.3648 (2)	4.70 (5)
C(14)	−0.2206 (3)	0.0816 (3)	0.3502 (1)	3.92 (4)
C(15)	−0.1009 (3)	0.0418 (3)	0.4057 (1)	3.92 (4)
B	0.1875 (3)	0.2362 (3)	0.1556 (1)	2.75 (4)
H(11)	0.580 (4)	0.482 (3)	0.129 (2)	2.6 (5)*
H(21)	0.792 (4)	0.692 (3)	0.250 (2)	3.4 (6)*
H(31)	0.554 (3)	0.608 (3)	0.356 (1)	1.7 (5)*
H(41)	0.262 (3)	−0.094 (3)	0.099 (1)	2.2 (5)*
H(51)	0.277 (4)	−0.287 (3)	0.206 (2)	3.0 (6)*
H(61)	0.207 (3)	−0.126 (3)	0.337 (1)	1.9 (5)*
H(71)	−0.055 (3)	0.301 (3)	0.228 (1)	1.5 (4)*
H(72)	−0.035 (3)	0.377 (3)	0.156 (1)	0.9 (4)*
H(81)	−0.221 (4)	0.009 (3)	0.155 (2)	3.5 (6)*
H(82)	−0.366 (4)	0.130 (4)	0.160 (2)	3.5 (6)*
H(83)	−0.251 (6)	0.113 (5)	0.082 (2)	7 (1)*
H(91)	0.371 (4)	0.219 (3)	0.057 (2)	3.4 (6)*
H(92)	0.135 (4)	0.101 (3)	0.042 (2)	3.1 (6)*
H(101)	0.326 (5)	0.509 (4)	0.046 (2)	6.1 (9)*
H(102)	0.067 (4)	0.370 (4)	0.022 (2)	4.3 (7)*
H(103)	0.203 (4)	0.342 (4)	−0.034 (2)	3.7 (7)*
H(131)	−0.339 (4)	0.272 (3)	0.323 (1)	2.2 (5)*
H(132)	−0.270 (4)	0.294 (3)	0.413 (2)	3.2 (6)*
H(141)	−0.252 (4)	0.022 (3)	0.303 (2)	2.7 (6)*
H(151)	−0.068 (3)	−0.053 (3)	0.397 (2)	2.0 (5)*
H(152)	−0.103 (4)	0.080 (3)	0.460 (2)	2.6 (5)*

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. Starred values indicate atoms refined isotropically.

Discussion

The Structure of Ia. An ORTEP drawing of complex Ia is given in Figure 1. The complex crystallizes in a triclinic unit cell and was refined in the $P\bar{1}$ space group with one whole molecule comprising the asymmetric unit. All of the positions of the hydrogen atoms were located from difference maps and refined freely. If the allyl group is considered to occupy a single coor-

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Table III. Bond Distances and Angles for $[Et_2B(pz)_2](CO)_2(\eta^3\text{-}H_2CCHCH_2)Mo$ (Ia)[a]

		Bond Distances (Å)			
Mo–N(1)	2.181 (1)	C(13)–H(132)	0.90 (3)	C(5)–H(51)	0.91 (3)
Mo–N(3)	2.238 (2)	C(14)–H(141)	0.88 (3)	C(6)–H(61)	1.04 (3)
Mo–C(11)	1.937 (2)	C(15)–H(151)	0.86 (3)	C(7)–C(8)	1.530 (3)
Mo–C(12)	1.963 (2)	C(15)–H(152)	0.96 (3)	C(7)–B	1.629 (3)
Mo–C(13)	2.331 (2)	H(71)–C(7)	0.95 (2)	C(7)–H(72)	0.97 (2)
Mo–C(14)	2.235 (2)	N(2)–C(1)	1.340 (2)	C(8)–H(81)	0.97 (3)
Mo–C(15)	2.373 (2)	N(2)–B	1.579 (2)	C(8)–H(82)	1.08 (3)
Mo–H(71)	2.24 (2)	N(4)–C(4)	1.348 (3)	C(8)–H(83)	0.99 (4)
C(13)–C(14)	1.410 (4)	N(4)–B	1.581 (3)	C(9)–C(10)	1.534 (5)
C(14)–C(15)	1.395 (3)	C(1)–C(2)	1.382 (3)	C(9)–B	1.618 (3)
N(1)–N(2)	1.359 (2)	C(1)–H(11)	0.95 (3)	C(9)–H(91)	0.99 (3)
N(1)–C(3)	1.344 (2)	C(2)–C(3)	1.383 (3)	C(9)–H(92)	0.96 (2)
N(3)–N(4)	1.366 (2)	C(2)–H(21)	0.92 (2)	C(10)–H(101)	1.23 (3)
N(3)–C(6)	1.350 (3)	C(3)–H(31)	0.85 (2)	C(10)–H(102)	0.92 (3)
C(11)–O(11)	1.151 (3)	C(4)–C(5)	1.389 (4)	C(10)–H(103)	0.95 (3)
C(12)–O(12)	1.147 (3)	C(4)–H(41)	1.01 (3)		
C(13)–H(131)	1.03 (3)	C(5)–C(6)	1.390 (3)		
		Bond Angles (deg)			
N(1)–Mo–N(3)	80.19 (5)	Mo–N(3)–N(4)	118.4 (1)	C(4)–C(5)–C(6)	105.0 (2)
N(1)–Mo–C(11)	96.77 (7)	Mo–N(3)–C(6)	134.4 (2)	C(4)–C(5)–H(51)	126 (2)
N(1)–Mo–C(12)	86.37 (7)	N(4)–N(3)–C(6)	107.1 (2)	C(6)–C(5)–H(51)	129 (2)
N(1)–Mo–C(13)	140.79 (8)	Mo–C(11)–O(11)	178.3 (2)	N(3)–C(6)–C(5)	109.9 (2)
N(1)–Mo–C(14)	157.56 (7)	Mo–C(12)–O(12)	176.8 (2)	N(3)–C(6)–H(61)	123 (1)
N(1)–Mo–C(15)	158.12 (7)	Mo–C(13)–H(131)	119 (1)	C(5)–C(6)–H(61)	127 (1)
N(1)–Mo–H(71)	77.2 (5)	Mo–C(13)–H(132)	117 (2)	H(71)–C(7)–C(8)	107 (1)
N(3)–Mo–C(11)	99.27 (8)	C(14)–C(13)–H(313)	114 (1)	H(71)–C(7)–B	119 (1)
N(3)–Mo–C(12)	166.48 (7)	C(14)–C(13)–H(132)	121 (2)	H(71)–C(7)–H(72)	97 (2)
N(3)–Mo–C(13)	122.16 (6)	H(131)–C(13)–H(132)	111 (2)	C(8)–C(7)–B	114.2 (2)
N(3)–Mo–C(14)	89.20 (7)	Mo–C(14)–H(141)	102 (2)	C(8)–C(7)–H(72)	106 (1)
N(3)–Mo–C(15)	83.72 (7)	C(13)–C(14)–H(141)	118 (2)	B–C(7)–H(72)	111 (1)
N(3)–Mo–H(71)	84.8 (6)	C(15)–C(14)–H(141)	123 (2)	C(7)–C(8)–H(81)	108 (2)
C(11)–Mo–C(12)	80.7 (1)	Mo–C(15)–H(151)	114 (2)	C(7)–C(8)–H(82)	114 (1)
C(11)–Mo–C(13)	109.05 (9)	Mo–C(15)–H(152)	113 (1)	C(7)–C(8)–H(83)	116 (2)
C(11)–Mo–C(14)	104.46 (8)	C(14)–C(15)–H(151)	120 (2)	H(81)–C(8)–H(82)	102 (2)
C(11)–Mo–C(15)	71.25 (8)	C(14)–C(15)–H(152)	122 (2)	H(81)–C(8)–H(83)	115 (3)
C(11)–Mo–H(71)	172.2 (5)	H(151)–C(15)–H(152)	122 (3)	H(82)–C(8)–H(83)	100 (3)
C(12)–Mo–C(13)	69.91 (9)	N(1)–N(2)–C(1)	108.8 (1)	C(10)–C(9)–B	115.6 (2)
C(12)–Mo–C(14)	103.95 (9)	N(1)–N(2)–B	119.2 (1)	C(10)–C(9)–H(91)	107 (2)
C(12)–Mo–C(15)	108.84 (8)	C(1)–N(2)–B	131.9 (2)	C(10)–C(9)–H(92)	111 (2)
C(12)–Mo–H(71)	93.8 (6)	N(3)–N(4)–C(4)	109.1 (2)	B–C(9)–H(91)	109 (2)
C(13)–Mo–C(14)	35.90 (9)	N(3)–N(4)–B	118.6 (1)	B–C(9)–H(92)	105 (2)
C(13)–Mo–C(15)	60.98 (9)	C(4)–N(4)–B	131.7 (2)	H(91)–C(9)–H(92)	108 (2)
C(13)–Mo–H(71)	73.9 (6)	N(2)–C(1)–C(2)	109.1 (2)	C(9)–C(10)–H(101)	111 (2)
C(14)–Mo–C(15)	35.09 (8)	N(2)–C(1)–H(11)	117 (1)	C(9)–C(10)–H(102)	115 (2)
C(14)–Mo–H(71)	82.2 (5)	C(2)–C(1)–H(11)	134 (1)	C(9)–C(10)–H(103)	115 (2)
C(15)–Mo–H(71)	116.1 (5)	C(1)–C(2)–C(3)	104.9 (2)	H(101)–C(10)–H(102)	110 (3)
Mo–C(13)–C(14)	68.3 (1)	C(1)–C(2)–H(21)	128 (2)	H(101)–C(10)–H(103)	109 (2)
Mo–C(14)–C(13)	75.8 (1)	C(3)–C(2)–H(21)	127 (2)	H(102)–C(10)–H(103)	97 (3)
Mo–C(14)–C(15)	77.9 (1)	N(1)–C(3)–C(2)	109.7 (2)	N(2)–B–N(4)	103.9 (1)
C(13)–C(14)–C(15)	116.6 (2)	N(1)–C(3)–H(31)	121 (1)	N(2)–B–C(7)	108.8 (1)
Mo–C(15)–C(14)	67.0 (1)	C(2)–C(3)–H(31)	129 (1)	N(2)–B–C(9)	111.1 (1)
Mo–N(1)–N(2)	119.60 (8)	N(4)–C(4)–C(5)	108.8 (2)	N(4)–B–C(7)	109.6 (1)
Mo–N(1)–C(3)	132.5 (1)	N(4)–C(4)–H(41)	119 (2)	N(4)–B–C(9)	109.6 (2)
N(2)–N(1)–C(3)	107.4 (1)	C(5)–C(4)–H(41)	132 (2)	C(7)–B–C(9)	113.4 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

dination site bonded through the center atom, C(14) (see Figure 1), the complex can be considered as having a roughly octahedral geometry. The other ligands bonded directly to the molybdenum atom are the two cis-CO groups, the two nitrogen atoms of the diethylbis(1-pyrazolyl)borate ligand, N(3) trans to C(12) and N(1) trans to C(14), and the hydrogen atom H(71), which is involved in the C–H···M interaction.

This geometry is analogous to that of complex Ib,[1] where the substituted allyl group $H_2CCPhCH_2$ occurs. A comparison of important bond distances and angles is given for Ia and Ib in Table IV. There are slight differences in the M–C(14) distances for the molybdenum to allyl bond in these two complexes. This is probably attributable to the steric and/or electronic interactions of the phenyl group on the allyl ligand in Ib.

Another notable difference is the slightly shorter Mo to B distance in Ia, 3.252 (2) Å, as compared with that in Ib, 3.290 (7) Å. Such distances were previously pointed out to be important characteristics of the C–H···M interaction associated with the dipyrazolylborate chelate ring, for much larger distances, ca. 3.8 Å, are observed if such interactions are absent.[13c] The decrease in Ia may be due to a reduction in steric interactions between the methyl group attached to the carbon atom involved in the C–H···M interaction and the substituent on the allyl ligand, which in the case of Ib is a phenyl group.[1]

The other bond distances listed in Table IV are equivalent within the uncertainties implied by their standard deviations. Most of the angles listed in Table IV are also equivalent, and this is a further confirmation of the isostructural nature of these two complexes.

One common aspect of the geometry of all these complexes[1,3,5,13] is the orientation of the allyl group relative to the rest of the

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(13) (a) Cotton, F. A.; Murillo, C. A.; Stults, B. R. *Inorg. Chim. Acta* **1977**, *22*, 75. (b) Cotton, F. A.; Frenz, B. A.; Murillo, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2118. (c) Cotton, F. A.; Frenz, B. A.; Stanislowski, A. *Inorg. Chim. Acta* **1973**, *7*, 503.

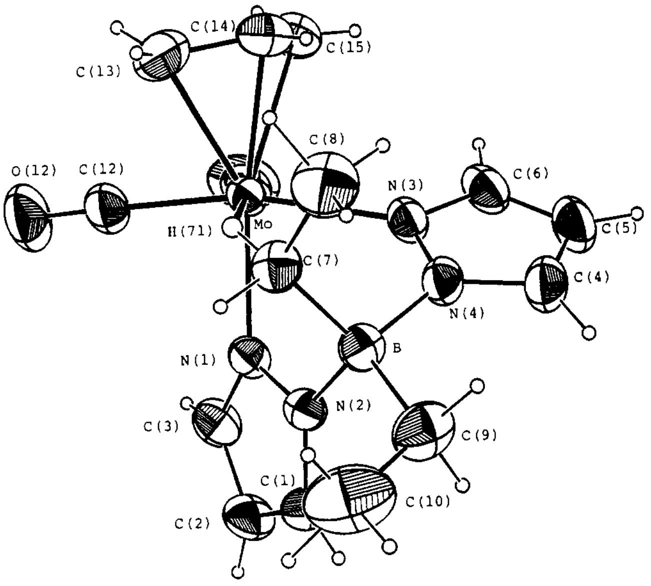

Figure 1. ORTEP drawing of Ia showing the full atomic labeling scheme. The ellipsoids represent thermal displacements and are drawn at the 50% probability level. The hydrogen atoms are represented by spheres of arbitrary size.

Table IV. Comparison of Important and Equivalent Bond Distances and Angles in Complexes Ia and Ib[a]

atoms	Ia	Ib
	Bond Distances (Å)	
Mo–N(1)	2.181 (1)	2.161 (5)
Mo–N(3)	2.238 (2)	2.209 (5)
Mo–C(11)	1.937 (2)	1.928 (7)
Mo–C(12)	1.963 (2)	1.942 (7)
Mo–C(13)	2.331 (2)	2.310 (7)
Mo–C(14)	2.235 (2)	2.260 (6)
Mo–C(15)	2.373 (2)	2.349 (7)
Mo–H(71)	2.24 (2)	2.27 (8)
Mo–C(7)	2.954 (2)	3.055 (6)
Mo–B	3.252 (2)	3.290 (7)
	Bond Angles (deg)	
N(1)–Mo–C(11)	96.77 (7)	97.8 (3)
N(1)–Mo–C(12)	86.37 (7)	82.4 (3)
N(1)–Mo–C(14)	157.56 (7)	158.5 (2)
N(1)–Mo–N(3)	80.19 (5)	81.1 (2)
N(1)–Mo–H(71)	77.2 (5)	77 (2)
N(3)–Mo–C(11)	99.27 (8)	95.0 (2)
N(3)–Mo–C(12)	166.48 (7)	162.0 (3)
N(3)–Mo–C(14)	89.20 (7)	96.2 (2)
N(3)–Mo–H(71)	84.8 (6)	78 (2)
C(11)–Mo–C(12)	80.7 (1)	80.2 (3)
C(11)–Mo–C(14)	104.46 (8)	103.7 (3)
C(11)–Mo–H(71)	172.2 (5)	172 (2)
C(12)Mo–C(14)	103.95 (9)	101.8 (3)
C(12)–Mo–H(71)	93.8 (6)	105 (2)
C(14)–Mo–H(71)	82.2 (5)	81 (2)
C(13)–Mo–C(14)	35.90 (9)	35.5 (3)
C(13)–Mo–C(15)	60.98 (9)	60.5 (3)
C(14)–Mo–C(15)	35.09 (8)	35.6 (3)
B–C(7)–C(8)	114.2 (2)	116.3 (6)
B–C(7)–H(71)	119 (1)	114 (5)
C(8)–C(7)–H(71)	106 (1)	106 (5)
Mo–H(71)–C(7)	131 (2)	136 (6)

[a] Data obtained from ref 1.

ligands. As one looks down the C″–Mo bond, where C″ is the middle carbon atom in the allyl ligand, C′C″C‴, this ligand is seen as approximately superposed on the OC–Mo–CO unit. This arrangement is probably favored because it results in the maximum orbital overlap between the filled metal d orbitals (i.e. the d_{xz} and d_{yz} orbitals if one considers the allyl ligand to be on the z axis) and the π^* orbitals on the allyl ligands.

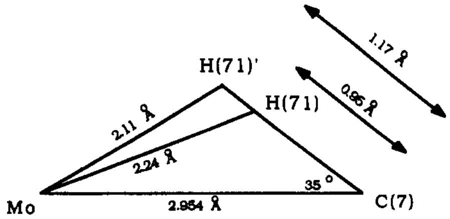

Figure 2. Schematic representation of the C–H···M interaction that shows the interatomic distances involving C(7), H(71), and Mo and the C(7)–H(71)′ and Mo–H(71)′ distances on the assumption that d(C(7)–H(71)′) = 1.17 Å and all other distances remain the same.

In the present work the data permitted us to obtain far better information about all hydrogen atoms, including the one of particular interest, H(71), than was the case with 1b,[1] where only 13 of the 25 hydrogen atoms were actually located in the difference maps and only one was refined in an unconstrained manner. The results for all of them except H(71) may be summarized in terms of C–H distances (Å) as follows: ring C–H (6×), 0.85 (2)–1.04 (3), average 0.95; allyl C–H (5×), 0.86 (3)–1.03 (3), average 0.93; alkyl C–H (8×), 0.92 (3)–1.08 (3), average 0.98 (outlying value of 1.23 omitted from average). The relatively low individual esd's for all of these and their consistency are quite exceptional. The overall average value, 0.96 Å, is typical of those generally obtained when CH hydrogen atoms can be detected and successfully refined in X-ray structures.

The hydrogen atom of prime importance here, H(71), the one in the C–H···Mo unit, has a position entirely consistent with those of all of the others; it is 0.95 (2) Å from C(7). Its distance from the Mo atom is 2.24 (2) Å. However, we may, as has been done before, invoke the idea that the "true" C–H distance is really considerably longer than the X-ray value, namely, about 1.10 Å, or we might even refer to the C–H distances found by neutron diffraction in other C–H···M cases, viz., ca. 1.17 Å. If we use a H(71)′ hydrogen atom (Figure 2) placed at one of these greater distances (but in the same direction) from C(7) we will, of course, calculate shorter Mo···H distances, namely, 2.11–2.13 Å.

What Is a Hydrogen Atom? There is a kind of conventional wisdom that neutron diffraction finds hydrogen atoms better than X-ray diffraction does. But is this even a meaningful statement, let alone a true one? It can be argued that it is not meaningful and thus incapable of being true. The simple facts are that neutrons and X-rays see two different parts of the hydrogen atom and that these parts do not coincide. It is then a Solomonic question whether either technique is justifiably considered to "see" the hydrogen atom. The neutron experiment sees, with considerable accuracy (ca. ±0.001 Å), the location of the hydrogen atom's *nucleus, the proton.* In a very favorable case such as we have here, the X-ray experiment sees, with less accuracy (ca. ±0.02 Å), the hydrogen atom's *electron cloud.* Which of these is "*the* hydrogen atom"? Both the nucleus and the electron density of an atom are essential parts, and it is therefore impossible to assert rationally that the position of either the one or the other is "the" position of the atom. Thus, the structure of a C–H···M interaction obtained by X-ray diffraction (provided decent accuracy, e.g., ±0.02 Å, is obtained) is just as valid in its way as a neutron diffraction study is in another way.

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Supplementary Material Available: Tables listing all crystallographic data and anisotropic displacement parameters for Ia and a stereoview of the crystal packing and unit cell (4 pages); a listing of observed and calculated structure factors for Ia (21 pages). Ordering information is given on any current masthead page.