

An Alkyne Derivative of an Organoimido Molybdenum(IV) Complex: Molecular Structure of the Acetone Hemi-solvate of Bis(diethyldithiocarbamato)-dimethylacetylenedicarboxylate(*p*-tolylimido)molybdenum(IV), Mo(Ntol)(DMAC)(S₂CNEt₂)₂·1/2Me₂CO

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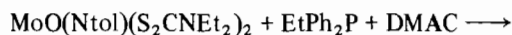
Abstract

The molecular structure of the dimethylacetylenedicarboxylate adduct of bis(diethyldithiocarbamato)-(*p*-tolylimido)molybdenum(IV), Mo(Ntol)(DMAC)(S₂CNEt₂)₂, is described. The complex represents a rare example of an unsaturated organic molecule ligated to an organoimido species. Crystals suitable for X-ray diffraction were obtained as the acetone hemi-solvate. The complex crystallizes in space group *P*2₁/*c* with the following parameters: *a* = 17.680(3), *b* = 8.860(1), *c* = 20.497(3) Å, β = 106.97(1)°, *Z* = 4. Least-squares refinement based on all 4039 unique intensities converged to *R* = 0.042 and *R*_w = 0.054. The complex displays a distorted pentagonal bipyramidal structure with the imido ligand occupying an apical position and the alkyne lying in the pentagonal plane. Analysis of the metrical parameters of the complex leads to the conclusion that the alkyne successfully contributes a slight amount of pi-electron density to the Mo atom in competition with the imido ligand.

Introduction

In recent years, the chemistry of transition metal organoimido complexes has burgeoned [1]. In part, this increased activity reflects a desire to use these complexes as reagents for delivery of an NR ligand to organic substrates, thus mimicking the well-known transfers of the isoelectronic oxo ligand [2]. Indeed, high-valent metal organoimido species have been strongly implicated as the active agents in two recent reports of olefin aziridination [3, 4]. However, there are few documented examples of unsaturated organic molecules acting as ligands in organoimido com-

plexes: apart from the ethylene and styrene complexes of the type Ta(NPh)(PMe₃)₃(olefin) [5], and the species [W(PhC≡CPh)Cl₂(dme)]₂(μ-N₂) [6] (dme = 1,2-dimethoxyethane), which contains a 'di-imido-like (μ-N₂⁴⁻)' ligand [7], the only other example known to us is the alkyne complex Mo(Ntol)(DMAC)(S₂CNEt₂)₂ [8] (tol = *p*-tolyl; DMAC = MeO₂CC≡CCO₂Me), which is prepared by generating the reactive Mo(IV) species Mo(Ntol)(S₂CNEt₂)₂ in the presence of the alkyne, as shown in eqn. (1). As part of our continuing investigations of transition



metal organoimido species [8–10], we report herein the molecular structure of the acetone hemi-solvate of Mo(Ntol)(DMAC)(S₂CNEt₂)₂.

Experimental

Data Collection and Reduction

Crystals of the title compound were obtained as previously described [8]. Intensity measurements were made on a Syntex P2₁ diffractometer using graphite (002) monochromatized MoKα radiation (λ = 0.71069 Å). A correction was applied for a small amount of decay (ca. 6%) observed in the intensity of three standard reflections during the period of data collection. Intensities were corrected for absorption [11a] and Lorentz-polarization factors (ideally imperfect crystal approximation assumed for the monochromator) and averaged for symmetry-related reflections (*Ok**l* and *Ok* – *l*). Reflections with *I*_o < 0.2σ(*I*_o) were reset to *I*_o = 0.2σ(*I*_o). All unique data were used in the subsequent refinement. Experimental details are presented in Table I.

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TABLE I. Summary of Crystallographic Data

Formula	MoS ₄ N ₃ O ₄ C ₂₃ H ₃₃ · $\frac{1}{2}$ C ₃ H ₆ O
Formula weight	668.75
Crystal dimensions (mm)	0.41 × 0.18 × 0.05
<i>a</i> (Å)	17.680(3)
<i>b</i> (Å)	8.860(1)
<i>c</i> (Å)	20.497(3)
β (deg)	106.97(1)
<i>V</i> (Å ³)	3071.1(8)
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	1.446
Space group	C _{2h} ⁵ - P2 ₁ /c
Radiation	Mo K α , λ = 0.71069 Å, mono-chromatized with highly oriented graphite
μ (cm ⁻¹)	7.18
<i>T</i> (°C)	25 ± 2
Scan range	1.0° below K α ₁ to 1.2° above K α ₂
Reflections measured	+ <i>h</i> , + <i>k</i> , ± <i>l</i> for 2 θ = 4.0 to 45.0°
Scan speed (deg min ⁻¹)	1.0 to 20.0
Take off angle (°)	4.0
Background counting	0.5 of net scanning time
Total measurements	4885 reflections
Unique measurements	4039 reflections
Number of variables	386
<i>R</i> ^a	0.042
<i>R_w</i> ^a	0.054

$$^aR = [\sum |F_o| - k|F_c| / \sum |F_o|]; \quad R_w = [\sum w(|F_o| - k|F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

Structure Solution and Refinement

The structure was determined by the heavy atom method. All hydrogen atoms except for those of the methyl groups of C27, C31, C35 and those in the acetone molecule were located in the difference maps. The positions of all hydrogens were idealized (C-H = 1.0 Å) assuming sp²- and sp³-hybridization of their carbon atoms. All positional and anisotropic thermal parameters of the non-hydrogen atoms and the isotropic thermal parameters for H-atoms (except those of the acetone molecule) were refined by two block-matrix least-squares procedures*; the quantity minimized was $\sum w(|F_o| - k|F_c|)^2$, where *w* refers to the weights and *k* is the scale factor (final value of *k* = 0.995(2)). In the early refinements, weights of $w = 4F_o^2/\sigma^2(F_o^2)$ were used. In later refinements, weights were taken as $w = 1/\sigma_{new}^2$, where $\sigma_{new}^2 = \sigma^2 + 0.5A|F_o|^2 + 0.5B(\sin \theta/\lambda)^2$; the values of A and B were obtained by least-squares minimization of the functions $\Sigma(\Delta F^2 - \sigma_{new}^2)^2$ for 20 separate segments in $|F_o|$ and $(\sin \theta/\lambda)$. The acetone molecule

*Scale, type I isotropic extinction [11b], and thermal parameters were put into one block while positional parameters were placed in another block. All calculations were performed on a Honeywell 66/6000 computer at the University of Kansas using programs in the DNA system written by F. Takusagawa (1984).

was found to be disordered around the center of symmetry. Thus, these atoms were assigned a 0.5 occupancy factor and their positions were varied with a restrained least-squares method (idealized distances: C36-O37 = 1.220; C36-C38 = 1.475; C36-C39 = 1.475; O37-C38 = 2.382; O37-C39 = 2.382; C38-C39 = 2.446 Å). Atomic scattering factors for Mo and S were taken from the usual source [12]. A difference map calculated after the final least-squares refinement was featureless. Fractional coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table II.

TABLE II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Mo	0.25897(2)	0.18041(4)	0.31623(2)	2.89
S2	0.15014(6)	0.1965(1)	0.36706(6)	3.79
S3	0.13473(7)	0.0572(1)	0.23754(6)	4.27
S4	0.33659(7)	0.0314(1)	0.25373(5)	3.64
S5	0.28541(6)	-0.0941(1)	0.36351(6)	3.51
N6	0.2489(2)	0.3279(4)	0.2583(2)	3.31
C7	0.3172(2)	0.2865(5)	0.4094(2)	3.20
C8	0.3707(2)	0.2259(5)	0.3886(2)	3.15
C9	0.0887(2)	0.1045(5)	0.2973(2)	3.63
N10	0.0135(2)	0.0799(4)	0.2913(2)	4.45
C11	-0.0400(3)	0.0077(6)	0.2296(3)	5.75
C12	-0.0836(4)	0.1262(8)	0.1789(4)	8.17
C13	-0.0210(3)	0.1218(7)	0.3450(3)	5.84
C14	-0.0200(4)	-0.0064(9)	0.3937(4)	8.15
C15	0.3404(2)	-0.1186(5)	0.3078(2)	3.10
N16	0.3815(2)	-0.2420(4)	0.3057(2)	3.63
C17	0.3838(3)	-0.3676(5)	0.3539(2)	4.18
C18	0.4446(3)	-0.3444(6)	0.4223(3)	5.21
C19	0.4283(3)	-0.2572(6)	0.2577(3)	5.00
C20	0.5097(4)	-0.1909(8)	0.2844(3)	7.05
C21	0.2405(2)	0.4122(5)	0.1994(2)	3.26
C22	0.2350(3)	0.5676(5)	0.1997(2)	3.86
C23	0.2252(3)	0.6489(5)	0.1397(3)	4.45
C24	0.2202(3)	0.5767(6)	0.0790(2)	4.58
C25	0.2256(4)	0.4234(7)	0.0792(3)	6.02
C26	0.2355(4)	0.3398(6)	0.1385(3)	5.47
C27	0.2075(4)	0.6652(7)	0.0126(3)	6.62
C28	0.3031(2)	0.3875(5)	0.4610(2)	3.68
O29	0.2542(3)	0.4844(6)	0.4483(2)	8.93
O30	0.3504(2)	0.3648(4)	0.5218(2)	5.38
C31	0.3428(4)	0.4677(7)	0.5744(3)	6.42
C32	0.4561(2)	0.2094(5)	0.3985(2)	3.39
O33	0.4951(2)	0.3040(4)	0.3816(2)	5.24
O34	0.4836(2)	0.0779(4)	0.4261(2)	4.36
C35	0.5678(3)	0.0524(6)	0.4382(3)	5.42
C36	-0.0090(8)	0.036(2)	-0.0090(8)	14.61
O37	-0.0463(8)	0.141(2)	-0.0413(6)	19.24
C38	0.0768(7)	0.047(2)	0.0269(8)	12.54
C39	-0.043(1)	-0.116(2)	-0.009(1)	18.80

$$^aB_{eq} = 8\pi^2 \langle U \rangle^2.$$

Results and Discussion

An ORTEP representation of the structure of Mo(Ntol)(DMAC)(S₂CNEt₂)₂ is given in Fig. 1, along with the atomic numbering scheme. Selected intramolecular bond distances and angles are collected in Table III. The complex adopts a distorted pentagonal bipyramidal geometry, in which the apical positions contain the *p*-tolylimido ligand and one of the sulfur atoms (S5) of a chelating dithiocarbamate ligand. As predicted from solution ¹H NMR studies [8], the alkyne is bound *cis* to the imido ligand and in the equatorial plane perpendicular to the Mo–N6 bond. Because of the small bite angle presented by the dithiocarbamate ligand, the N6–Mo–S5 angle (157.69(13)°) is decidedly non-linear. As expected, the molybdenum atom is displaced from the pentagonal plane toward the nitrogen atom [by 0.314(1) Å].

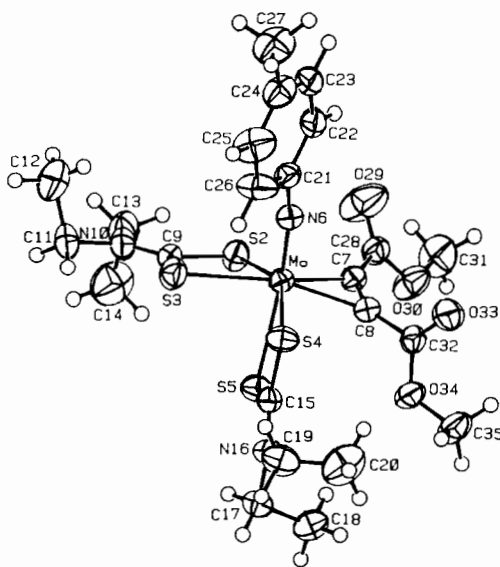
The bonding within the dithiocarbamate chelates is typical of that usually displayed by these ligands. Thus, excluding the terminal methyl groups, the dithiocarbamate skeletons are nearly planar and the C15–N16 and C9–N10 bond lengths of 1.32 Å reflect partial double bond character in these linkages.

The Mo–N6 bond length of 1.740(3) Å is very close to the average Mo–NR distance of 1.73 Å found in three eighteen-electron molybdenum-imido complexes: Mo(NPh)Cl₂(S₂CNEt₂)₂ (1.734(4) Å) [13]; [(η⁵-C₅H₅)Mo(N^tBu)]₂(μ-S)₂ (1.733(4) Å) [14]; Mo(Ntol)Cl₂(Me₇PhP)(PhCON=Ntol) (1.726(9) Å) [15]. This distance suggests considerable triple bond character in the Mo–N bond. Thus, to a first approximation, we may regard Mo(Ntol)(DMAC)(S₂CNEt₂)₂ as an eighteen-electron species if we consider the imido ligand to donate four electrons and the alkyne to contribute two electrons. However, there appears to be slightly too much bending about the tolylimido nitrogen atom to conform exactly to this description: the Mo–N6–C21 angle is 163.79(31)°. Most of this bending is attributable to uneven N–Mo ππ–dπ overlap as is commonly encountered in related pentagonal bipyramidal species, but the present value is some 5° less obtuse than the average angle of 168.7° observed in three similar complexes: Nb(Ntol)(S₂CNEt₂)₃ [16] (Nb–N–C = 167.4(3)°); [Mo(NNEtPh)(S₂CN(CH₂)₅)₃]⁺ [17] (Mo–N–N = 170(2)°); Mo(NPh)Cl₂(S₂CNEt₂)₂ [13] (Mo–N–C = 166.8(3)°).

The bending of the tolylimido group is directed between the Mo–S4 and the Mo–S3 bond vectors: the dihedral angle about Mo–N6 is 33.5° with respect to S4 and 54.7° with respect to S3. Furthermore, the plane containing the six phenyl carbon atoms is virtually coincident with the plane of bending: the angle between the Mo–N6–C21 plane and the phenyl plane is 1.34°.

TABLE III. Selected Bond Distances (Å) and Angles (°) in Mo(Ntol)(DMAC)(S₂CNEt₂)₂

Distances			
Mo–S2	2.445(1)	S2–C9	1.728(4)
Mo–S3	2.559(1)	S3–C9	1.708(5)
Mo–S4	2.509(1)	S4–C15	1.719(4)
Mo–S5	2.610(1)	S5–C15	1.715(5)
Mo–N6	1.740(3)	N6–C21	1.389(5)
Mo–C7	2.107(4)	C9–N10	1.316(6)
Mo–C8	2.134(4)	C15–N16	1.320(5)
C7–C8	1.264(6)		
Angles			
Mo–N6–C21	163.79(31)	S3–Mo–C7	149.71(13)
N6–Mo–C7	102.08(15)	S3–Mo–C8	165.63(11)
N6–Mo–C8	102.85(15)	S5–Mo–S2	88.51(4)
N6–Mo–S2	108.11(13)	S5–Mo–S3	82.20(4)
N6–Mo–S3	89.54(10)	S5–Mo–S4	68.50(4)
N6–Mo–S4	90.51(13)	S5–Mo–C8	83.62(11)
N6–Mo–S5	157.69(13)	S5–Mo–C7	95.29(11)
C7–Mo–S2	79.91(13)	C7–C8–C32	146.61(38)
S2–Mo–S3	68.88(4)	C8–C7–C28	143.67(37)
S3–Mo–S4	87.16(4)	Mo–C7–C28	141.98(29)
S4–Mo–C8	85.49(13)	Mo–C8–C32	141.37(32)
C8–Mo–C7	34.69(17)		

Fig. 1. ORTEP drawing of the structure of Mo(Ntol)(DMAC)(S₂CNEt₂)₂. Thermal ellipsoids are drawn at the 50% probability level.

The mean Mo–S distance for the three equatorial sulfur atoms is 2.504 Å, a value very close to the respective average Mo–S distances found in MoOCl₂(S₂CNEt₂)₂ [18] (2.50 Å) and in Mo(NPh)Cl₂(S₂CNEt₂)₂ [13] (2.51 Å). The Mo–S5 bond *trans* to the tolylimido ligand is considerably longer at

TABLE IV. Selected Structural Parameters for Monomeric Molybdenum Alkyne Complexes

Complex ^a	Mo–C (Å)	C≡C (Å)	C≡C–R (°)	Formal e [−] -donation	Reference
Mo(Ntol)(DMAC)(S ₂ CNEt ₂) ₂	2.107(4) 2.134(4)	1.264(4)	143.67(37) 146.61(38)	~2.5	this work
Mo(η ⁵ -C ₅ H ₅) ₂ (PhC≡CPh)	2.143(6) 2.144(6)	1.269(7)	–	~2	22
MoO(S ₂ CNMe ₂) ₂ (tolCOC≡CCOtol)	2.122(4) 2.119(4)	1.267(6)	149.3(4) 149.7(4)	~2.5	23
MoO(η ⁵ -C ₅ H ₅)(SC ₆ F ₅)(F ₃ CC≡CCF ₃)	2.082(8) 2.109(8)	1.267(12)	137.7(9) 142.5(10)	~2.5	24
Mo(^t BuS) ₂ (^t BuNC) ₂ (HC≡CH)	2.04(2) 2.05(2)	1.28(2)	143(2) 152(2)	4	25 ^b
Mo(CO)(PEt ₃) ₂ Br ₂ (PhC≡CH)	1.988(10) 1.982(9)	1.273(11)	134.0(9) 139(4)	4	26
Mo(CO)(η ⁵ -C ₅ H ₅)(SC ₆ F ₅)(F ₃ CC≡CCF ₃)	2.017(5) 2.051(5)	1.298(6)	136.6(5) 137.8(5)	4	24
Mo(TPP)(PhC≡CPh)	1.983(4) 1.965(4)	1.324(5)	136.4(4)	4	22

^aAbbreviations used: tol = *p*-tolyl; Ph = C₆H₅; Me = CH₃; Et = C₂H₅; DMAC = dimethylacetylenedicarboxylate; TPP = meso-tetraphenylporphyrinato; ^tBu = tert-butyl. ^bSee also footnote 9b of reference 26.

2.610(1) Å. Even when one corrects for the inherent lengthening of the axial distance (*ca.* 0.06 Å for Mo) [16] induced by the small bite angle of the spanning dithiocarbamate, the Mo–S5 distance is still approximately 0.05 Å longer than expected. This small, but significant, apparent *trans*-influence exerted by the tolylimido ligand in this complex is intriguing because previous work has shown that imido ligands in six- and seven-coordinate eighteen-electron complexes do not exert a *trans*-influence [1]. Imido ligands have, however, been shown to exert a *trans*-influence in two distinct classes of complexes: electron-deficient species (such as sixteen-electron Mo(Ntol)Cl₄(THF) [10] and seventeen-electron W(NPh)Cl₃(PPh₃)₂ [19]) and, more appositely, in electron-excessive species characterized by bent imido ligands such as Mo(NPh)₂(S₂CNEt₂)₂ [20] and MoO(NH)Cl₂(OPEtPh₂)₂ [21].

The small discrepancies observed regarding both the *trans*-influence and the bending of the tolylimido ligand can be accounted for by invoking a slight degree of competition between the imido and alkyne ligands for pi-donation into a mutually available d-orbital on Mo. The structural parameters of the DMAC ligand support this contention.

Table IV summarizes pertinent details of the Mo–alkyne interactions in Mo(Ntol)(DMAC)(S₂CNEt₂)₂ and several other monomeric molybdenum alkyne complexes. The C≡C bond lengths in this series are relatively insensitive to changes in either the substituents or formal electron donation number of the alkyne as well as to changes in the oxidation

state and coordination geometry of the complexes. A rather smooth correlation is observed however between the formal number of electrons donated by the alkyne and the molybdenum to alkyne carbon bond length. Thus, the average Mo–C distance for the four ‘four-electron donor’ alkyne complexes is 2.01 Å, a value much shorter than the respective distance of 2.143 Å observed in the ‘two-electron donor’ complex Mo(η⁵-C₅H₅)₂(PhC≡CPh). The corresponding average Mo–C distance in Mo(Ntol)(DMAC)(S₂CNEt₂)₂ is 2.12 Å, consistent with the alkyne providing slightly more than two electrons in this complex. The bonding in this complex can be accounted for as follows. If the symmetry is idealized to be C_s and a coordinate system is defined such that the z-axis lies along the Mo–N6 bond vector and the y-axis bisects the midpoint of the C≡C bond, then the filled in-plane alkyne π_{xy} orbital can overlap with an spd hybrid orbital of Mo directed along y, while the vacant alkyne π_{xy}^{*} orbital can accept electron density from the filled Mo d_{xy} orbital. The filled nitrogen p_x and p_y orbitals can form two pi bonds by overlap with the vacant d_{xz} and d_{yz} orbitals, respectively, of Mo. These interactions lead to four electron donation by the imido ligand and two electron donation by the alkyne. However, the second filled π orbital of the alkyne (π_{xz}) is also of the appropriate symmetry to donate into the Mo d_{yz} orbital [23, 27] and thus must compete with the p_y orbital of nitrogen. Successful pi donation from π_{xz} to Mo will force electron density back into Np_y and is manifest in the following

structural observations: shortening of the Mo–C distance (*ca.* 0.02 Å), lengthening of the Mo–N6 bond (*ca.* 0.01 Å), bending of the tolylimido ligand (5°) and the *trans*-lengthening of Mo–S5 (0.05 Å). Viewed individually, each of these changes is small enough so as not to be particularly significant; taken collectively, however, the fact that all of the parameters shift in accordance with the above scheme suggests that the above description is a reasonable one.

Acknowledgements

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Supplementary Material

Anisotropic thermal parameters (Table V), observed and calculated structure factor amplitudes (Table VI), complete intramolecular bond lengths (Table VII) and bond angles (Table VIII), and positional and thermal parameters of hydrogen atoms (Table IX) (32 pages). This information has been deposited and is available from the Editor-in-Chief.

References

- 1 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, **31**, 123 (1980).
- 2 R. A. Sheldon and J. K. Kochi, 'Metal-Catalyzed Oxidations of Organic Compounds', Academic Press, New York, 1981.
- 3 J. T. Groves and T. Takahashi, *J. Am. Chem. Soc.*, **105**, 2073 (1983).
- 4 D. Mansuy, J.-P. Mahy, A. Durreault, G. Bedi and P. Battioni, *J. Chem. Soc., Chem. Commun.*, 1161 (1984).
- 5 S. M. Rocklage and R. R. Schrock, *J. Am. Chem. Soc.*, **104**, 3077 (1982).
- 6 M. R. Churchill, Y.-J. Li, K. H. Theopold and R. R. Schrock, *Inorg. Chem.*, **23**, 4472 (1984).
- 7 (a) M. R. Churchill and H. J. Wasserman, *Inorg. Chem.*, **20**, 2899 (1981); (b) *Inorg. Chem.*, **21**, 218 (1982); (c) S. M. Rocklage, H. W. Turner, J. D. Fellmann and R. R. Schrock, *Organometallics*, **1**, 703 (1982).
- 8 D. D. Devore and E. A. Maatta, *Inorg. Chem.*, in press.
- 9 E. A. Maatta, *Inorg. Chem.*, **23**, 2560 (1984).
- 10 C. Y. Chou, J. C. Huffman and E. A. Maatta, *J. Chem. Soc., Chem. Commun.*, 1184 (1984).
- 11 (a) A. C. T. North, D. C. Phillips and F. S. Matthews, *Acta Crystallogr., Sect. A*, **24**, 351 (1984); (b) P. J. Becker and P. Coppens, *Acta Crystallogr., Sect. A*, **31**, 417 (1975).
- 12 D. T. Cromer and J. T. Waber (eds.), 'International Tables for X-ray Crystallography, Vol. IV', Kynoch Press, Birmingham, 1974.
- 13 E. A. Maatta, B. L. Haymore and R. A. D. Wentworth, *Inorg. Chem.*, **19**, 1055 (1980).
- 14 L. F. Dahl, P. D. Frisch and G. R. Gust, 'Proc. Int. Conf. Chem. Uses Molybdenum, Reading, U.K., 1973', Vol. 1, Climax Molybdenum, London, 1974, p. 134.
- 15 M. W. Bishop, J. Chatt, J. R. Dilworth, M. B. Hursthouse, S. A. A. Jayaweera and A. Quick, *J. Chem. Soc., Dalton Trans.*, 914 (1979).
- 16 L. S. Tan, G. V. Goeden and B. L. Haymore, *Inorg. Chem.*, **22**, 1744 (1983).
- 17 F. C. March, R. Mason and K. M. Thomas, *J. Organomet. Chem.*, **96**, C45 (1975).
- 18 J. Dirand, L. Ricard and R. Weiss, *J. Chem. Soc., Dalton Trans.*, 278 (1976).
- 19 D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, A. J. Nielson and R. L. Short, *J. Chem. Soc., Dalton Trans.*, 2651 (1983).
- 20 B. L. Haymore, E. A. Maatta and R. A. D. Wentworth, *J. Am. Chem. Soc.*, **101**, 2063 (1979).
- 21 J. Chatt, R. Choukroun, J. R. Dilworth, J. Hyde, P. Vella and J. Zubieta, *Transition Met. Chem.*, **4**, 59 (1979).
- 22 A. DeCian, J. Colin, M. Schappacher, L. Ricard and R. Weiss, *J. Am. Chem. Soc.*, **103**, 1850 (1981).
- 23 W. E. Newton, J. W. McDonald, J. L. Corbin, L. Ricard and R. Weiss, *Inorg. Chem.*, **19**, 1997 (1980).
- 24 J. A. K. Howard, R. F. D. Stansfield and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 246 (1976).
- 25 M. Kamata, T. Yoshida, S. Otsuka, K. Hirotsu, T. Higuchi, M. Kido, K. Tatsumi and R. Hoffmann, *Organometallics*, **1**, 227 (1982).
- 26 P. B. Winston, S. J. N. Burgmayer and J. L. Templeton, *Organometallics*, **2**, 167 (1983).
- 27 (a) K. Tatsumi, R. Hoffman and J. L. Templeton, *Inorg. Chem.*, **21**, 466 (1982); (b) B. C. Ward and J. L. Templeton, *J. Am. Chem. Soc.*, **102**, 1532 (1980); (c) J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, **102**, 3288 (1980).