

Table 3. Comparison of bond and torsion angles ( $^{\circ}$ ) for [TcO(NEt-tmdadt)] and [TcO(NH-tmdadt)]

Bond angles	[TcO(NEt-tmdadt)]	[TcO(NH-tmdadt)]*
S(1)—Tc—O	108.3 (1)	109.3 (2)
N(2)—Tc—O	104.7 (1)	101.1 (3)
S(1)—Tc—N(2)	146.7 (1)	149.3 (3)
S(2)—Tc—O	115.6 (1)	117.0 (3)
N(1)—Tc—O	114.4 (1)	117.8 (4)
S(2)—Tc—N(1)	129.6 (1)	124.4 (3)
Torsion angles†		
S(1)C(1)C(4)N(1)	N(1)C(5)C(6)N(2)	N(2)C(9)C(10)S(2)
[TcO(NEt-tmdadt)]	-40.9	46.4
[TcO(NH-tmdadt)]*	-41.1	53.6

\* Epps (1984).

† Since a glide plane exists, there are mirror image molecules which have these angles with the signs reversed.

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## Structure of Dicarbonyl( $\eta$ -cyclopentadienyl)( $N,N'$ -diphenylacetamidinato)-molybdenum(II), [Mo(C<sub>5</sub>H<sub>5</sub>)(C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>)(CO)<sub>2</sub>]

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**Abstract.** [C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub>{C<sub>6</sub>H<sub>5</sub>NC(CH<sub>3</sub>)NC<sub>6</sub>H<sub>5</sub>}], C<sub>21</sub>H<sub>18</sub>MoN<sub>2</sub>O<sub>2</sub>,  $M_r = 426.33$ , triclinic,  $P\bar{1}$ ,  $a = 9.683$  (4),  $b = 10.873$  (5),  $c = 11.161$  (5) Å,  $\alpha = 94.87$  (3),  $\beta = 123.56$  (4),  $\gamma = 102.10$  (3) $^{\circ}$ ,  $V = 928$  (1) Å<sup>3</sup>,  $D_m = 1.51$  (1) Mg m<sup>-3</sup>,  $Z = 2$ ,  $D_x = 1.526$  (2) Mg m<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 0.707$  mm<sup>-1</sup>,  $F(000) = 432$ ,  $T = 293$  K,  $R = 0.032$  for 3067 unique observed reflections. The amidino group bonds to Mo in a symmetrical bidentate mode, with the metal lying in the ligand skeletal NCN plane. The Mo atom is coordinated to 2N at 2.17–2.18 Å, to 2C (carbonyl) at 1.94–1.95 Å, and 5C (Cp) at 2.28–2.41 Å. Skeletal C–N distances are short (1.32 Å). Crystal packing is layered, with adjacent molecules within the layers having opposite orientations.

**Introduction.** Complexes of the type [C<sub>5</sub>H<sub>5</sub>M(CO)<sub>2</sub>{R'NC(R)NR'}] ( $M = \text{Mo, W}$ ,  $R' = \text{aryl}$ ,  $R = \text{Ph, H, CH}_3$ ) were first synthesized from C<sub>5</sub>H<sub>5</sub>M(CO)<sub>3</sub>X ( $X = \text{halide}$ ) using amidines or their metallo-derivatives (Inglis & Kilner, 1975; Gaylani & Kilner, 1976; de Roode & Vrieze, 1978). The amidinato-group here acts as a 3-electron ligand, which may be accomplished by  $N,N'$ -chelation, by bridging between two metals in a binuclear or larger unit, or by C,N-chelation by an *ortho*-metallated group (Barker, Cameron, Kilner, Mahmoud & Wallwork, 1986; Cotton, Inglis, Kilner & Webb, 1975; Barker, Kilner, Mahmoud & Wallwork, 1989). The structures of a series of chiral benzamidinato-complexes [R''C<sub>5</sub>H<sub>4</sub>Mo(CO)<sub>2</sub>{R'NC(R)NR'}] [ $R = \text{C}_6\text{H}_5$ ,  $R' = \text{CH}(\text{C}_6\text{H}_5)Y$ , where  $Y = \text{H, CH}_3$ ,  $R'' = \text{H}$ ,

## References

- BAIDOO, K. E. (1988). PhD Thesis, The Johns Hopkins Univ., Baltimore, Maryland, USA.
- BANDOLI, G., MAZZI, U., RONCARI, E. & DEUTSCH, E. (1982). *Coord. Chem. Rev.* **44**, 191–227.
- DAVISON, A., ORVIG, C., TROP, H. S., SOHN, M., DEPAMPHILIS, B. V. & JONES, A. G. (1980). *Inorg. Chem.* **19**, 1988–1992.
- DEPAMPHILIS, B. V., JONES, A. G., DAVIS, M. A. & DAVISON, A. (1978). *J. Am. Chem. Soc.* **100**, 5570–5571.
- EPPS, L. A. (1984). PhD Thesis, The Johns Hopkins Univ., Baltimore, Maryland, USA.
- JONES, A. G., DAVISON, A., LATÉGOLA, M. R., BRODACK, J. W., ORVIG, C., SOHN, M., TOOTHAKER, A. K., LOCK, C. J. L., FRANKLIN, K. J., COSTELLO, C. E., CARR, S. A., BIEMANN, K. & KAPLAN, M. L. (1982). *J. Nucl. Med.* **23**, 801–809.
- LEVER, S. Z., SUN, S.-Y., KALTOVICH, F., SCHEFFEL, U., GOLDFARB, H., MAHMOOD, A., BAIDOO, K. E. & WAGNER, H. N. JR (1988). *J. Nucl. Med.* **29**, 789.
- PINKERTON, T. C., DISLETS, C. P., HOCK, D. J., MIKELSON, M. V. & WILSON, G. M. (1985). *J. Chem. Educ.* **62**, 965–973.
- SHELDRICK, G. M. (1984). *SHELXTL Users Manual*. Revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.
- WATSON, A. D., TULIP, T. H. & ROE, D. C. (1986). In *Technetium in Chemistry and Nuclear Medicine 2*, edited by M. NICOLINI, G. BANDOLI & U. MAZZI, pp. 61–63. New York: Raven.

CH<sub>3</sub>], related to the title acetamidinato complex, have since been reported (Creswick & Bernal, 1983; Bernal, Creswick, Brunner & Agrifogli, 1980).

**Experimental.** C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>Cl (0.50 g, 1.78 mmol) and C<sub>6</sub>H<sub>5</sub>NC(CH<sub>3</sub>)NHC<sub>6</sub>H<sub>5</sub> (0.75 g, 3.57 mmol) in toluene (35 cm<sup>3</sup>) were stirred at 323–328 K for 9.5 h, during which time the colour changed from orange to orange-brown and a white precipitate separated. After filtration of the solution, reduction in volume (293 K, *in vacuo*) and cooling to 253 K orange crys-

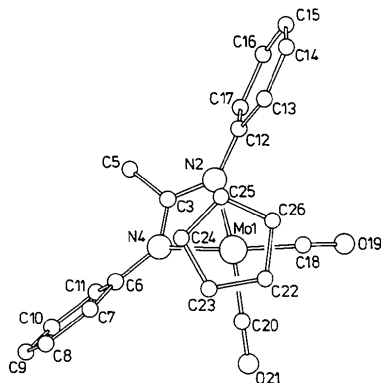


Fig. 1. The molecular structure projected onto the plane of the cyclopentadienyl ring.

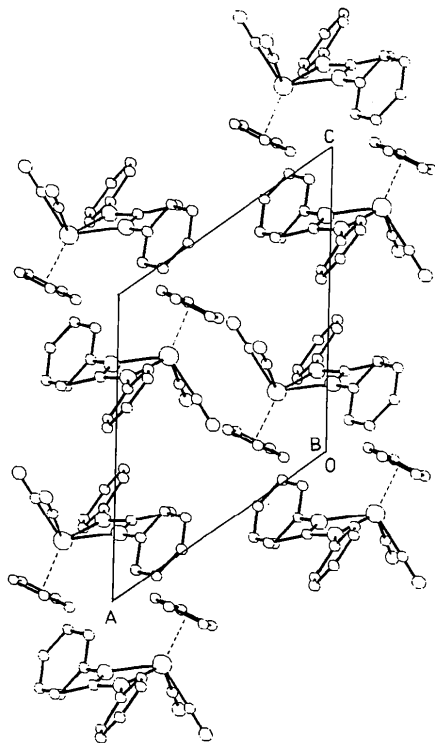


Fig. 2. The crystal structure projected along the *b* axis.

Table 1. Atomic coordinates and isotropic or equivalent isotropic thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> )
Mo(1)	0.24216 (3)	0.18053 (2)	0.31671 (3)	0.0400 (4)
N(2)	0.0521 (3)	0.0140 (3)	0.2938 (3)	0.040 (3)
N(4)	-0.0268 (3)	0.1752 (3)	0.2113 (3)	0.043 (4)
C(3)	-0.0815 (4)	0.0598 (3)	0.2266 (4)	0.041 (4)
C(5)	-0.2660 (5)	-0.0116 (4)	0.1656 (5)	0.056 (5)
C(6)	-0.1267 (4)	0.2587 (3)	0.1481 (4)	0.045 (4)
C(7)	-0.1083 (5)	0.3228 (4)	0.0535 (5)	0.057 (5)
C(8)	-0.2058 (7)	0.4043 (5)	-0.0126 (6)	0.073 (7)
C(9)	-0.3218 (7)	0.4237 (6)	0.0152 (7)	0.090 (9)
C(10)	-0.3374 (8)	0.3631 (6)	0.1127 (8)	0.097 (11)
C(11)	-0.2396 (6)	0.2810 (5)	0.1802 (6)	0.071 (7)
C(12)	0.0502 (4)	-0.1077 (3)	0.3301 (3)	0.040 (4)
C(13)	0.1461 (5)	-0.1759 (4)	0.3123 (4)	0.048 (5)
C(14)	0.1436 (6)	-0.2975 (4)	0.3408 (5)	0.059 (5)
C(15)	0.0483 (6)	-0.3511 (4)	0.3909 (6)	0.070 (6)
C(16)	-0.0415 (7)	-0.2826 (5)	0.4130 (7)	0.078 (7)
C(17)	-0.0392 (6)	-0.1595 (4)	0.3861 (5)	0.059 (6)
C(18)	0.3774 (4)	0.1687 (3)	0.5227 (4)	0.045 (4)
O(19)	0.4568 (4)	0.1634 (3)	0.6445 (3)	0.070 (4)
C(20)	0.2937 (5)	0.3495 (3)	0.4314 (5)	0.051 (5)
O(21)	0.3269 (5)	0.4493 (3)	0.5014 (5)	0.085 (5)
C(22)	0.4721 (4)	0.2517 (4)	0.3044 (4)	0.048 (5)
C(23)	0.3270 (5)	0.2767 (4)	0.1820 (5)	0.054 (5)
C(24)	0.2032 (5)	0.1572 (5)	0.0838 (4)	0.059 (5)
C(25)	0.2686 (5)	0.0579 (4)	0.1440 (4)	0.056 (5)
C(26)	0.4331 (5)	0.1156 (4)	0.2805 (4)	0.051 (5)

Table 2. Bond lengths (Å) and selected bond angles (°)

Mo—N(2)	2.176 (3)	C(9)—C(10)	1.378 (7)
Mo—N(4)	2.169 (3)	C(10)—C(11)	1.393 (6)
Mo—C(18)	1.952 (4)	C(6)—C(11)	1.382 (5)
Mo—C(20)	1.943 (4)	C(12)—N(2)	1.416 (4)
Mo—C(22)	2.282 (3)	C(12)—C(13)	1.386 (5)
Mo—C(23)	2.302 (3)	C(12)—C(17)	1.382 (5)
Mo—C(24)	2.393 (4)	C(13)—C(14)	1.385 (5)
Mo—C(25)	2.411 (3)	C(14)—C(15)	1.380 (6)
Mo—C(26)	2.325 (3)	C(15)—C(16)	1.359 (7)
C(3)—N(2)	1.320 (4)	C(16)—C(17)	1.394 (6)
C(3)—N(4)	1.320 (4)	C(20)—O(21)	1.150 (5)
C(3)—C(5)	1.498 (5)	C(18)—O(19)	1.148 (4)
C(6)—N(4)	1.407 (4)	Mo—N(2)—C(3)	96.4 (2)
C(6)—C(7)	1.383 (5)	Mo—N(4)—C(3)	96.7 (2)
C(7)—C(8)	1.383 (6)	Mo—N(2)—C(12)	137.0 (2)
C(8)—C(9)	1.369 (7)	Mo—N(4)—C(6)	136.8 (2)
N(2)—Mo—N(4)	58.9 (1)	C(10)—C(11)—C(6)	119.8 (4)
N(2)—Mo—C(18)	82.4 (1)	C(12)—C(13)—C(14)	120.7 (3)
N(4)—Mo—C(20)	83.8 (1)	C(13)—C(12)—C(17)	118.7 (3)
N(2)—C(3)—N(4)	108.0 (3)	C(13)—C(14)—C(15)	120.2 (4)
C(5)—C(3)—N(2)	126.0 (3)	C(14)—C(15)—C(16)	119.2 (4)
C(5)—C(3)—N(4)	125.8 (3)	C(15)—C(16)—C(17)	121.4 (4)
C(3)—N(2)—C(12)	126.6 (3)	C(16)—C(17)—C(12)	119.6 (4)
C(3)—N(4)—C(6)	126.5 (3)	Mo—C(18)—O(19)	179.0 (3)
N(2)—C(12)—C(13)	118.4 (3)	Mo—C(20)—O(21)	178.8 (4)
N(2)—C(12)—C(17)	122.9 (3)	C(22)—C(23)—C(24)	108.4 (3)
N(4)—C(6)—C(7)	118.9 (3)	C(23)—C(22)—C(26)	106.8 (3)
N(4)—C(6)—C(11)	122.2 (3)	C(23)—C(24)—C(25)	108.1 (3)
C(6)—C(7)—C(8)	120.8 (4)	C(24)—C(25)—C(26)	108.0 (3)
C(7)—C(6)—C(11)	118.9 (3)	C(25)—C(26)—C(22)	108.6 (3)
C(7)—C(8)—C(9)	120.5 (4)	N(2)—Mo—C(20)	119.2 (1)
C(8)—C(9)—C(10)	119.2 (4)	N(4)—Mo—C(18)	118.2 (1)
C(9)—C(10)—C(11)	120.8 (4)	C(18)—Mo—C(20)	75.3 (2)

tals of the present complex separated. Recrystallization was from diethyl ether. The white precipitate was identified by elemental analysis *etc.* as C<sub>6</sub>H<sub>5</sub>NHC(CH<sub>3</sub>)NHC<sub>6</sub>H<sub>5</sub><sup>+</sup>.Cl<sup>-</sup>. Density measured by flotation in xylene/carbon tetrachloride mixtures.

After preliminary X-ray photography, lattice parameters were refined from 16 reflections with  $11^\circ < \theta < 14^\circ$  and about 3300 X-ray intensities were measured on a Hilger & Watts computer-controlled, four-circle diffractometer up to  $\theta = 25^\circ$  using a  $\theta/2\theta$  scan technique in the range  $-11 \leq h \leq 9$ ,  $-12 \leq k \leq 12$ ,  $0 \leq l \leq 12$ . Of these, 3067 were regarded as significant [ $I > 3\sigma(I)$ ]. No corrections were made for absorption, in view of the low absorption coefficient and small crystal size (maximum dimension *ca* 0.5 mm). The structure was solved by the heavy-atom Patterson method, and refined by least-squares calculations (on *F*), using anisotropic thermal parameters, to a final *R* value of 0.032, *wR* = 0.044. H atoms were included in calculated positions with fixed isotropic thermal parameters, and not refined. A weighting scheme of the form of a four-term Chebyshev polynomial was applied in the last few cycles of refinement (235 parameters refined).  $\Delta/\sigma_{\max} = 0.14$ . The *CRYSTALS* system of programs was employed.

**Discussion.** A drawing of the molecular structure showing the atomic numbering scheme is given in Fig. 1. Table 1 gives the atomic coordinates and *U*<sub>eq</sub> values for the non-H atoms and Fig. 2 shows the crystal structure projected along the *b* axis.\*

The bond distances and angles found for the present complex (Table 2) correspond closely to those found for the related chiral benzamidinato complexes, except for features relating to the chiral

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53448 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

centres, and the substituent at the skeletal C atom. The skeletal NCN angle is generally lower (108.0°) when the latter substituent is methyl, than when it is phenyl (usually 110–112°), except for the case where each N atom substituent is CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>. Also for this acetamidinato complex the Mo atom is positioned, within experimental error, in the skeletal NCN plane whereas for the chiral complexes dihedral angles up to 5.7° occur. The planes of the phenyl rings of the present complex are twisted so that two *ortho*-H atoms lie below the plane containing the metal and skeletal NCN atoms, whereas the methyl C atom lies above this plane, thus minimizing repulsion. The packing of the molecules in the crystal is in layers parallel to (10 $\bar{1}$ ), with adjacent molecules within the layers in opposite orientations.

We thank the Science and Engineering Research Council for supplying the X-ray diffractometer.

#### References

- BARKER, J., CAMERON, N. J., KILNER, K., MAHMOUD, M. M. & WALLWORK, S. C. (1986). *J. Chem. Soc. Dalton Trans.* pp. 1359–1365.  
 BARKER, J., KILNER, M., MAHMOUD, M. M. & WALLWORK, S. C. (1989). *J. Chem. Soc. Dalton Trans.* Accepted for publication.  
 BERNAL, I., CRESWICK, M. W., BRUNNER, H. & AGRIFOGLIS, G. (1980). *J. Organomet. Chem.* **198**, C4.  
 CARRUTHERS, J. R. & WATKIN, D. J. (1980). *CRYSTALS*. Oxford Univ. Computing Laboratory, Oxford, England.  
 COTTON, F. A., INGLIS, T., KILNER, M. & WEBB, T. R. (1975). *Inorg. Chem.* **14**, 2023–2026.  
 CRESWICK, M. W. & BERNAL, I. (1983). *Inorg. Chim. Acta*, **74**, 241–269.  
 GAYLANI, B. & KILNER, M. (1976). *J. Less Common Met.* **54**, 175.  
 INGLIS, T. & KILNER, M. (1975). *J. Chem. Soc. Dalton Trans.* pp. 930–934.  
 ROODE, W. H. DE & VRIEZE, K. (1978). *J. Organomet. Chem.* **153**, 345–357.

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## 1-Carbonyl-1- $\eta^5$ -cyclopentadienyl-2,2,2-triphenyl-1-triphenylphosphine- $\mu$ -carboxylato-1 $\kappa$ C:2 $\kappa$ O:2 $\kappa$ O'-iron(III)

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**Abstract.** [FeSn(C<sub>5</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(CO)(CO<sub>2</sub>){P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}]<sub>2</sub>, *M<sub>r</sub>* = 805.27, orthorhombic, *Pbca*, *a* =

17.972 (2), *b* = 20.254 (4), *c* = 20.148 (3) Å, *V* = 7334.0 Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.46 g cm<sup>-3</sup>, Mo *K*α (*λ* = 0.71073 Å), *μ* = 11.60 cm<sup>-1</sup>, *F*(000) = 3264, *T* = 296 K, 5282 unique reflections, *R* = 0.038, *wR* =

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