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Amidine and guanidine complexes of manganese and molybdenum. Crystal structures of (η-cyclopentadienyl)(*N*,*N*′-diphenylguanidino)- and (η-cyclopentadienyl)(*N*,*N*′,*N*″-triphenylguanidino)-dicarbonylmolybdenum(II)

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Reactions of *N*,*N*′-diphenyl- and *N*,*N*′,*N*″-triphenylguanidine with $[MnBr(CO)_5]$ gave *cis*-[MnBr{PhNC(NHR)NHPh}$(CO)_4$], *fac*-[MnBr{PhNC(NHR)NHPh}$_2(CO)_3$] and [Mn{PhNC(NHR)NPh}$(CO)_4$] (R = H or Ph), the last complex being formed at higher temperatures with an excess of ligand. In reactions of these guanidines with $[MoCl(\eta\text{-}C_5H_5)(CO)_3]$, HCl was eliminated and $[Mo(\eta\text{-}C_5H_5)$\{PhNC(NHR)NPh\}$(CO)_2$] complexes (R = H or Ph) formed. Crystal structures of these molybdenum complexes have been determined, revealing symmetrically chelating co-ordination of the guanidino ligands (in close semblance of corresponding amidino-complexes) with the four-membered metallacycle planar for R = Ph but unusually (by 21°) folded for R = H due to hydrogen bonding of an uncommon type. Reaction of lithio-*N*,*N*′-di-*p*-tolylbenzamidine with $[Mo(\eta\text{-}C_7H_7)(CO)_3]BF_4$ yielded [Mo{η-$C_7H_7N(p\text{-}MeC_6H_4)C(Ph)NC_6H_4Me$-*p*}$(CO)_3$], consistent with nucleophilic attack at the ring, followed by nitrogen co-ordination at the metal by a pendant amidine group.

Amidines RNHC(R′)=NR and their deprotonated anions display a great variety of modes of co-ordination with transition metals[1] and interesting isoelectronic and isostructural relationships with other pseudo-allylic ligands, namely triazines, carboxylates, dithiocarboxylates, dithiocarbamates, dithiophosphates and diselenophosphonates.[2] Guanidines, *i.e.* amidine derivatives with an amino-substituent R′, seem even more promising, being stronger electron donors than amidines[3] and apparently possessing all the co-ordination possibilities of the latter plus another potential co-ordination centre in the form of the third nitrogen atom. On the other hand, it was supposed[4] that electron delocalisation over the N_3C moiety should actually impair the co-ordinating ability of the nitrogen atoms by making their lone pairs more diffuse. The first complexes of transition metals (Co, Cu, Zn, Pd and Ni) with 1,1,3,3-tetramethylguanidine (tmg) were reported long ago[5] and the monodentate two-electron co-ordination of tmg through the imine nitrogen atom was postulated on the basis of the IR spectra. Such co-ordination was later confirmed by X-ray diffraction studies in the complexes of Tc with tmg[4] and of Pt with $HN{=}C(NEt_2)_2$.[6] Of the substituted guanidines, cyanoguanidine recently became popular as a ligand, capable of terminal, bridging and chelating co-ordination.[7] Guanidino, *i.e.* deprotonated guanidine, ligand can give more sophisticated modes of co-ordination, similar to those of amidines.[1] In particular, a bridging $HNC(NH_2)NH$ anion[8] and a chelating PhNC(=NPh)NPh dianion[9] were observed in structurally characterised platinum complexes.

We have found earlier[10] that amidines RNHC(R′)=NR (R = Ph or *p*-tolyl; R′ = H, Me or Ph) and their lithio-derivatives RN(Li)C(R′)=NR react with $[MnBr(CO)_5]$ **1** and $[MoCl(\eta\text{-}C_5H_5)(CO)_3]$ **2** to form complexes of the [Mn{CON(R)C(R′)NR}$(CO)_4$], [Mn{RNC(R′)NR}$(CO)_4$] **3**, $[Mo(\eta\text{-}C_5H_5)$\{CON(R)C(R′)NR\}$(CO)_2$] and $[Mo(\eta\text{-}C_5H_5)$\{RNC(R′)NR\}$(CO)_2$] **4** types. The lithiated amidines attack a carbonyl ligand of both **1** and **2** to produce a carbamoyl group CON(R)C(R′)NR which acts as a three-electron chelate ligand, its subsequent decarbonylation yielding **3**[10a] or **4**.[10b,c] Complex **4** can be also obtained directly from RNHC(R′)=NR and **2**, the amidine readily losing the proton on co-ordination, especially with molybdenum. In the present work we studied the co-ordinating abilities of aryl-substituted guanidines in similar reactions with **1** and **2**, and extended the studies of amidine systems as well.

Results and Discussion

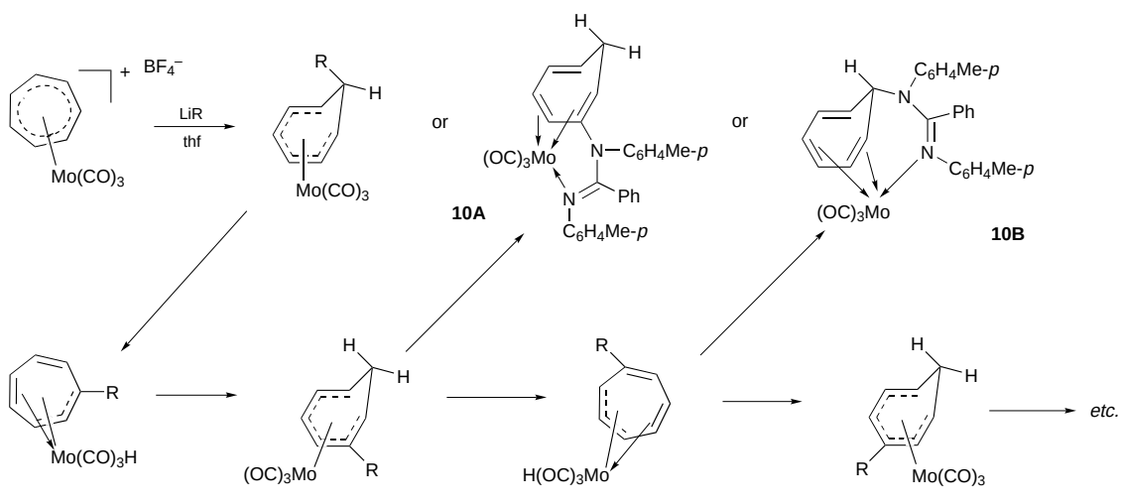
(*a*) Manganese carbonyl complexes

N,*N*′-Diphenyl- and *N*,*N*′,*N*″-triphenyl-guanidine react with complex **1** in a manner typical for monodentate two-electron donors,[11] displacing one and then another carbonyl group to form *cis*-[MnBr{PhNC(NHR)NHPh}$(CO)_4$] **5** and *fac*-[MnBr{PhNC(NHR)NHPh}$_2(CO)_3$] **6**, where R = H or Ph. We suppose that the guanidine ligands are co-ordinated *via* the imino nitrogen atom, as has been observed earlier.[4,6] The stereochemical configurations of **5** and **6** were assigned on the basis of the intensities and pattern of the ν(CO) stretching frequencies (see Table 1) and there was no evidence for isomerisation of the *fac* into the *mer* isomer of **6**, as occurs for bulkier ligands such as triphenylphosphine.[16] The ν(CN) stretching frequencies of the guanidine ligands remain virtually the same as those for the free guanidines and their complexes with other Lewis acids. Thus, ν(CN) in Nujol are 1636 cm^{-1} for $(PhNH)_2CNPh$, 1620–1625 for complexes **5** and **6** and 1638 cm^{-1} for $(PhNH)_2CNPh{\cdot}BF_3$.

When a two-fold excess of the guanidine is used in the reaction with complex **1** in toluene the guanidine acts also as a proton base, precipitating its hydrobromide salt and leaving [Mn{PhNC(NHR)NPh}$(CO)_4$] (R = H **7a** or Ph **7b**) in solution. The same reaction occurs during spontaneous decomposition of **6** in solutions. The guanidinium bromide released thereupon is probably the reason why the solutions of **6** in polar solvents behave as 1 : 1 electrolytes, *e.g.* with the molar conductivity of 91 $ohm^{-1}\ cm^2\ mol^{-1}$ in nitromethane [*cf.* 89 $ohm^{-1}\ cm^2\ mol^{-1}$ for $PhNC(NHPh)_2{\cdot}HBr$]. Complex **7b** was also synthesized in the metathetical reaction of **1** with lithio-*N*,*N*′,*N*″-triphenylguanidine in tetrahydrofuran (thf) solution, the presence or absence of $Me_2NCH_2CH_2NMe_2$ being of no consequence to the outcome of the reaction. However, attempts to

Table 1 ν(CO) Stretching frequencies of the prepared and related complexes

Complex	R	Form	$\tilde{\nu}$(CO)/cm^{-1}	Ref.
5a [MnBr{PhNC(NHR)NHPh}(CO)$_4$]	H	Nujol	2100m, 2030s, 2000s, 1960s	This work
5b	Ph	Nujol	2099w, 2030s, 2001s, 1958s	This work
6a [MnBr{PhNC(NHR)NHPh}$_2$(CO)$_3$]	H	Nujol	2010s, 1920s, 1895s	This work
	—	CH_2Cl_2	2091w, 2013s, 1990s, 1950s	This work
6b	Ph	Nujol	2012s, 1923s, 1898s	This work
7a [Mn{PhNC(NHR)NPh}(CO)$_4$]	H	Hexane	2092, 2011s, 1991s, 1949s	This work
7b	Ph	Nujol	2093m, 2010s, 1990s, 1933s	This work
[Mn{PhNC(R)NPh}(CO)$_4$]	Me	cyclo-C_6H_{12}	2096w, 2017s, 1996s, 1955s	10(*a*)
	Ph	cyclo-C_6H_{12}	2093w, 2010s, 1995s, 1950s	10(*a*)
[Mn($CF_3COCHCOCF_3$)(CO)$_4$]	—	$CHCl_3$	2123w, 2055s, 1973s, 1950s	12
[Mn(S_2CPh)(CO)$_4$]	—	CCl_4	2100w, 2022s, 2017 (sh), 1972s	13
[Mn(S_2PEt_2)(CO)$_4$]	—	C_6H_{14}	2092m, 2014s, 2000s, 1963s	14
[Mn{$S_2C_2(CN)_2$}(CO)$_4$]$^-$	—	$CHCl_3$	2075w, 2010s, 1982s, 1933m	15
8a [Mo(η-C_5H_5){PhNC(NHR)NPh}(CO)$_2$]	H	Nujol	1942s, 1848s	This work
8b	Ph	Nujol	1935s, 1830s	This work
	—	Et_2O	1915s, 1857s	This work
[Mo(η-C_5H_5){PhNC(R)NPh}(CO)$_2$]	Me	Toluene	1953s, 1859s	10(*c*)
	Ph	CCl_4	1970s, 1890s	10(*b*)
	—	Nujol	1950s, 1864 (sh), 1852s	10(*b*)
10 [Mo{C_7H_7(*p*-MeC_6H_4)NC(Ph)NC_6H_4Me-*p*}(CO)$_3$]	—	Nujol	1925s, 1840s, 1800s	This work



Scheme 1 Supposed rearrangements of cycloheptatrienylamidino molybdenum complexes; R = *p*-$MeC_6H_4NC(CHPh)NC_6H_4Me$-*p*

prepare the same complex from **5b** (R = Ph), using *n*-butyllithium or triethylamine were unsuccessful, and only **6b**, the product of the reaction of **5b** with additional free guanidine, was detected. The additional guanidine can arise only from decomposition of a portion of the starting complex, **5b**.

The guanidine and guanidino complexes are less stable in solution towards decomposition and air oxidation than the amidine and amidino complexes, but otherwise are similar to the latter in their properties and IR spectra (see Table 1), which suggest similar molecular structures. For **7**, as for corresponding amidino complexes, two structures are possible: mononuclear with a chelating NCN moiety or binuclear with bridging ones. From the available evidence (mass spectral study being unsuccessful) the structure cannot be assigned unequivocally but is more likely to be mononuclear, as in related complexes, in view of the similarity of the IR spectra (see Table 1).[10*a*–*c*,12–15]

(*b*) Cyclopentadienyl molybdenum complexes

Guanidines PhNC(NHR)NHPh react smoothly with complex **2** to form [Mo(η-C_5H_5){PhNC(NHR)NPh}(CO)$_2$] (R = H **8a** or Ph **8b**), substitution of a carbonyl group by the amidine being followed by elimination of HCl, captured by a second amidine molecule as the amidinium chloride. The intermediate complex, [MoCl(η-C_5H_5){PhNC(NHR)NHPh}(CO)$_2$], was not detected in the solution during the reaction. Compounds **8a** and **8b**, characterised by single-crystal structures (see below), both contain chelating three-electron guanidine ligands. The course of the reaction, the structure, properties and IR spectra (Table 1) of the products are similar to those observed for the corresponding amidines.

(*c*) Cycloheptatriene molybdenum complexes

Lithio-*N*,*N*′-di-*p*-tolylbenzamidine reacts with [Mo(η-C_7H_7)(CO)$_3$]BF_4 **9** in thf solution at −40 °C to produce a complex having the formal composition [Mo{η-C_7H_7(*p*-MeC_6H_4)NC(Ph)NC_6H_4Me-*p*}(CO)$_3$] **10**. Thus, the amidine enters the complex as the formally anionic amidino-group, while all three carbonyl ligands remain there in a facial arrangement, as indicated by three strong ν(CO) stretching frequencies in the IR spectrum of **10**. These frequencies (1925s, 1840s, 1800s cm^{-1}) are considerably lower than for [Mo(η-C_7H_8)(CO)$_3$] (1970s, 1910, 1860s cm^{-1} in Nujol),[17] as should be expected when a strong electron donor, such as the amidine nitrogen atom, enters the co-ordination sphere. The only possible explanation is that the lithioamidine attacks the cycloheptatrienyl ring with one nitrogen atom and then co-ordinates to the metal atom with another, in a strap-type structure (Scheme 1), while the cycloheptatrienyl co-ordination switches from η^6 to η^4.

The ^{1}H NMR spectrum of complex **10** contains signals due to aromatic protons (phenyl group) and C(sp^2)-bound cycloheptatrienyl protons [δ 7.25 (m), 7.1 (br m), 6.7 (t), 6.2 (dt) and 5.2 (dd)], an intense signal due to the methyl protons at δ 2.2,

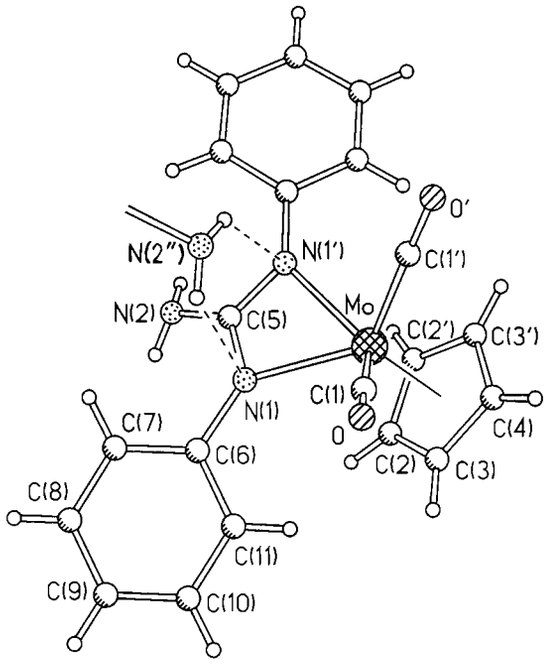


Fig. 1 Molecular structure of complex **8a**, showing the intermolecular hydrogen bonds. Primed atoms are symmetry-related *via* plane *m*, double primed *via* plane *a*

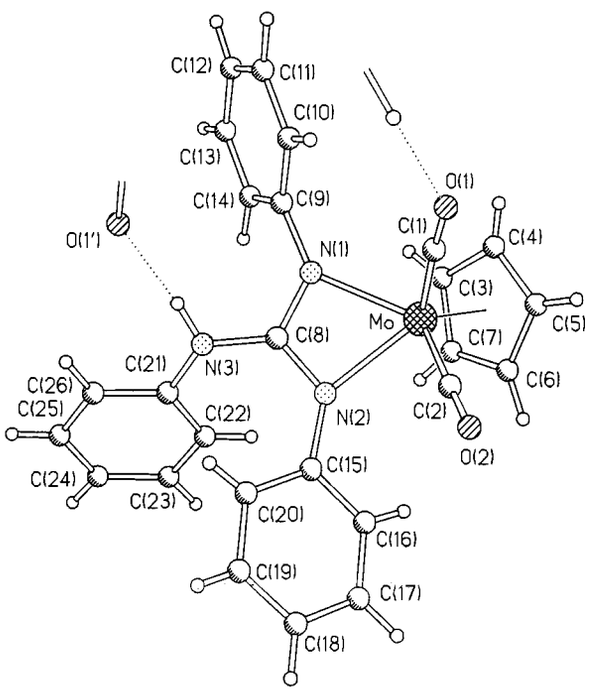


Fig. 2 Molecular structure of complex **8b**, showing intermolecular hydrogen bonds. Primed atoms are symmetry-related *via* an inversion centre

and two one-proton singlets, δ 2.3 (s) and 2.0 (s). The last two signals can be attributed respectively to the *exo*- and *endo*-protons of the cycloheptatrienyl CH_2 group, by analogy with the assignments for $[Co(\eta\text{-}C_7H_8)(PMe_3)]BPh_4$ [δ 2.0 (br) and 2.3 (s)][18] and $[Mo(\eta\text{-}C_7H_8)(CO)_3]$ (δ 2.40 and 3.01, respectively).[19] The structure most consistent with the available data is **10A** (Scheme 1), in which the amidino-bridge is bonded to one of the sp^2-carbon atoms of the cycloheptatrienyl ring. An alternative explanation, the presence of equal amounts of $[Mo(\eta\text{-}C_7H_7R)(CO)_3]$ isomers with the amidino (R) substituents in the *endo* and *exo* positions at the sp^3 carbon of the ring, seems implausible. In a η^6-cycloheptatriene ligand the sp^3 carbon atom is always bent out of the planar η^6 co-ordinated moiety

Table 2 Selected bond distances (Å) and angles (°) in complexes **8a** and **8b**

Complex **8a**			
Mo–N(1)	2.187(3)	Mo–Cp*	2.012(5)
Mo–C(1)	1.966(4)	N(1)–C(5)	1.336(4)
Mo–C(2)	2.399(4)	N(2)–C(5)	1.357(6)
Mo–C(3)	2.317(4)	N(1)–C(6)	1.414(4)
Mo–C(4)	2.296(5)		
N(1)–Mo–C(1)	86.5(1)	C(1)–Mo–C(1′)	74.4(2)
N(1)–Mo–Cp*	116.0(2)	N(1)–Mo–C(1′)	122.6(1)
C(1)–Mo–Cp	120.4(2)	Mo–N(1)–C(5)	94.0(2)
N(1)–C(5)–N(1′)	108.6(4)	N(1)–C(5)–N(2)	125.7(2)
N(1)–Mo–N(1′)	59.5(2)		
Complex **8b**			
Mo–N(1)	2.172(4)	Mo–N(2)	2.191(4)
Mo–C(1)	1.952(4)	Mo–C(2)	1.962(5)
Mo–C(3)	2.407(5)	Mo–C(7)	2.394(5)
Mo–C(4)	2.322(5)	Mo–C(6)	2.312(5)
Mo–C(5)	2.285(5)	Mo–Cp*	2.016(5)
N(1)–C(8)	1.327(6)	N(2)–C(8)	1.336(6)
N(1)–C(9)	1.427(6)	N(2)–C(15)	1.418(6)
N(3)–C(21)	1.413(5)	N(3)–C(8)	1.387(6)
N(1)–Mo–N(2)	59.8(1)	C(1)–Mo–C(2)	73.3(2)
N(1)–Mo–C(1)	86.9(2)	N(2)–Mo–C(2)	84.7(2)
N(1)–Mo–C(2)	121.9(2)	N(2)–Mo–C(1)	121.0(2)
N(1)–Mo–Cp	117.6(2)	N(2)–Mo–Cp	118.6(2)
C(1)–Mo–Cp	120.0(2)	C(2)–Mo–Cp	119.7(2)
N(1)–C(8)–N(2)	109.4(4)	C(8)–N(3)–C(21)	127.3(4)
N(1)–C(8)–N(3)	123.0(4)	N(2)–C(8)–N(3)	127.4(4)

* Cp = Centroid of the cyclopentadienyl ring.

and away from the metal atom.[20] Therefore the hypothetical structure of the *endo* isomer **10B** is much less favourable for strong Mo–N (amidino) co-ordination than **10A**, and in the *exo* isomer such co-ordination is altogether impossible. Hence the two isomers should exhibit very different ν(CO) stretching frequencies, while only one set of three bands is observed.

Reported reactions of complex **9** with Lewis bases (Nu) are of three types,[21] *i.e.* nucleophilic attacks at the metal centre (substituting one CO group for a Nu ligand), at the C_7H_7 ring (forming a η^6-C_7H_7Nu ligand), and at a carbonyl group [forming a C(=O)Nu ligand]. Under mild conditions hard bases (neutral or anionic) tend to react at the carbocyclic ring, and soft bases at the metal.[22] Thus the attack of the lithioamidine at the ring is not unusual. Its mechanism may be similar to the reaction of **9** with MeO^- ion in methanol, which proceeds through fast initial formation of an [Mo]–CO_2Me group or an $[Mo(\eta\text{-}C_7H_8)(CO)_3][OMe]$ ion pair to the irreversible formation of the C_7H_7OMe ligand.[23] Such reactions normally end with the nucleophile attached to the non-co-ordinated (sp^3) carbon atom of the η^6 ring. However, a 1,3-shift isomerisation process (shown in Scheme 1), well known for linear-chain alkenes[24] and similar to some processes observed in fused aromatic π ligands (*e.g.* ricochet inter-ring haptotropic rearrangements in dihydro[10]annulene complexes of tricarbonylchromium[25]), can change the position of the saturated carbon atom in the ring, leaving the amidino substituent at an sp^2 carbon atom. In principle, each position of the substituent with respect to the CH_2 group is accessible in this way, but from the NMR evidence it is the 3 isomer, shown in Scheme 1 (**10A**) which is formed. The equilibrium process of this interconversion does not manifest itself in the NMR spectrum, only one isomer being detected.

(*d*) Crystal structures of complexes 8a and 8b

The molecular structures of complexes **8a** and **8b** are similar (Figs. 1 and 2, Table 2). Molecule **8a** is situated on a crystallographic mirror plane, passing through the Mo, C(4), C(5) and N(2) atoms. In both complexes the Mo atoms lie at a distance

of 2.01 Å from the cyclopentadienyl ring plane and are chelated by the guanidino-ligand symmetrically (in **8a**) or almost symmetrically (in **8b**). The Mo–N distances are within the range usual for amidino complexes of the [Mo(η-C_5H_5){RNC(R′)NR}$(CO)_2$] type (2.15–2.20 Å).[10d,26] The chelation in such complexes is usually symmetrical: Mo–N distances never differ by more than 0.04 Å (*cf.* by 0.02 Å in **8b**) and often are crystallographically equivalent.

Both N(1) and N(1′) atoms of complex **8a** form (symmetry-related) hydrogen bonds with the $N(2)H_2$ group of another molecule, generated from the former one by a glide plane *a* [N(1) · · · N(2″) 3.131(6), N(2″)–H 0.83(3), H · · · N(1) 2.50(4) Å, N(2″)–H–N(1) 133(3)°], thus linking molecules into an infinite chain parallel to the crystallographic *x* axis. Although the bond is not particularly strong, it causes a substantial distortion of the planar trigonal (sp^2) bond geometry (characteristic for other amidino complexes[10d,26]) of N(1), which is displaced by 0.15 Å from the MoC(5)C(6) plane in the direction of the hydrogen bond. Consequently, the four-membered metallacycle, which is usually nearly planar, is folded along the N(1) · · · N(1′) vector by 21°. Of 90 structurally characterised amidino-complexes of various transition metals,[27] only four show folding angles (φ) as high as 15–19°, these being sterically overcrowded complexes with $Me_3SiNC(Ph)NSiMe_3$ ligands.[28] In all other complexes φ does not exceed 11°, and in the [Mo(η-C_5H_5){RNC(R′)NR}$(CO)_2$] complexes, it does not exceed 6°.

A three-co-ordinate sp^2-nitrogen atom forming a hydrogen bond is very uncommon. The Cambridge Structural Database[27] contains only one example of such an atom, participating in co-ordination with a metal and in multiple C–N bonds, to form any intermolecular N · · · H contact shorter than the sum of van der Waals radii (2.66 Å),[29] namely [V(η-C_5H_5)(*p*-MeC_6H_4-$NCHNC_6H_4Me$-*p*)$_2$][30] with a N · · · H (tolyl) contact of 2.58 Å. Characteristically, in the latter complex the nitrogen atom forming the hydrogen bond is noticeably more pyramidalised than the other (the sums of bond angles around them are 354.6 and 359.4°, respectively), and the metallacycle is folded by 11°.

In contrast, in complex **8b** the Mo, C(8) and three nitrogen atoms are essentially coplanar. The bulky phenyl substituent at N(3) causes the twist of *ca.* 32° around the C(8)–N(3) bond, interfering with the π delocalisation in the guanidino moiety. Thus, the C(8)–N(3) bond in **8b** is 0.03 Å longer than C(5)–N(2) bond in **8a**, while bond lengths in the chelating NCN moiety remain the same.

The amino group in complex **8b** forms an intermolecular hydrogen bond with one of the carbonyl groups [N(3) · · · O(1′) 2.995(5), N(3)–H 0.88(6), H · · · O(1′) 2.18(6) Å, N–H–O 154(5)°] of the molecule, symmetry-related to the former one *via* the inversion centre ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$).

Experimental

N,*N*′-Di-*p*-tolylbenzamidine was prepared by a published procedure[31] and recrystallised from toluene–hexane mixtures before use. *N*,*N*′-Diphenylguanidine and *N*,*N*′,*N*″-triphenylguanidine (Pfaltz and Bauer, Inc.) were recrystallised from toluene–hexane. Other chemicals were supplied by Aldrich. The complex [$MnBr(CO)_5$] **1** was prepared from [$Mn_2(CO)_{10}$], [MoCl(η-C_5H_5)$(CO)_3$][32] **2** and [Mo(η-C_7H_8)$(CO)_3$][17] from [Mo$(CO)_6$] using literature methods. Precautions were taken to exclude air and moisture; solvents were pre-dried, and degassed before use. Infrared spectra in the range 4000–250 cm^{-1} were recorded using a Perkin-Elmer 1600 spectrometer, ^1H NMR spectra at 250 MHz using a Bruker AC 250 spectrometer, using $SiMe_4$ as an internal standard. The carbon, hydrogen, and nitrogen contents of the complexes were determined using a Carlo Erba EMA 1106 elemental analyser.

Reactions

Complex 1 with *N*,*N*′,*N*″-triphenylguanidine. (*a*) Complex **1** (0.54 g, 1.96 mmol) was dissolved in toluene (40 cm^3) and solid *N*,*N*′,*N*″-triphenylguanidine (0.30 g, 1.04 mmol) added against a counterflow of nitrogen. The mixture was heated at 45–50 °C for 12 h, and produced a clear orange solution. On cooling to −10 °C the excess of **1** separated and was filtered off. Removal of solvent (20 cm^3) *in vacuo* from the solution, addition of hexane and cooling to −10 °C gave the product, [MnBr{PhNC(NHPh)$_2$}$(CO)_4$] **5b**, an air-stable yellow microcrystalline solid. Yield: 0.36 g (65% based on the guanidine). M.p. 115–117 °C (decomp.) (Found: C, 51.39; H, 3.11; Br, 14.43; N, 7.68. $C_{23}H_{17}BrMnN_3O_4$ requires C, 51.71; H, 3.21; Br, 14.96; N, 7.87%).

(*b*) A mixture of complex **1** (0.52 g, 1.9 mmol) and *N*,*N*′,*N*″-triphenylguanidine (1.09 g, 3.8 mmol), suspended in hexane (45 cm^3), was heated for 12 h at 45–50 °C. Carbon monoxide was evolved during the heating process. The yellow solid product, [MnBr{PhNC(NHPh)$_2$}$_2(CO)_3$] **6b**, precipitated and was separated from the reaction mixture by filtration, washed with hexane, and dried *in vacuo*. Yield: 1.12 g (75% based on **1**) (Found: C, 60.09; H, 4.26; Br, 10.02; N, 10.46. $C_{41}H_{34}BrMnN_6O_3$ requires C, 62.05; H, 4.32; Br, 10.07; N, 10.59%). M.p. 68–71 °C (decomp).

(*c*) Complex **1** (0.50 g, 1.8 mmol) was added to a solution of *N*,*N*′,*N*″-triphenylguanidine (1.04 g, 3.6 mmol) in toluene (30 cm^3), and the mixture slowly warmed to 50 °C. Eventually **1** dissolved, and with further heating a pale solid separated. Heating was continued for 6 h, after which time the solid was filtered off, washed with toluene and dried *in vacuo*. The white solid was identified as [PhNHC(NHPh)$_2$]Br by analysis and by comparison with an authentic sample (Found: C, 62.50; H, 4.89; N, 11.90. $C_{19}H_{18}BrN_3$ requires C, 61.97; H, 4.93; N, 11.41%). The filtrate was evaporated to dryness *in vacuo*, and the residue extracted with dichloromethane (3 × 10 cm^3). Evaporation of the filtered extracts to small bulk and cooling to −10 °C yielded yellow microcrystalline [Mn{PhNC(NHPh)NPh}$(CO)_4$] **7b**. Yield: 0.64 g (77%), based on **1** (Found: C, 60.96; H, 3.91; N, 9.96. $C_{23}H_{16}MnN_3O_4$ requires C, 60.94; H, 3.56; N, 9.27%).

Complex 1 with *N*,*N*′-diphenylguanidine. (*a*) The same method, as described in (*a*) above, using complex **1** (0.45 g, 1.6 mmol) and $PhNC(NH_2)NHPh$ (0.34 g, 1.6 mmol) yielded [MnBr{$PhNC(NH_2)NHPh$}$(CO)_4$] **5a**, as a yellow microcrystalline solid. Yield: 0.61 g, 81% (Found: C, 44.46; H, 3.02; N, 8.90. $C_{17}H_{13}BrMnN_3O_4$ requires C, 44.57; H, 2.86; N, 9.17%).

(*b*) The same reaction, as described in (*b*) above, using complex **1** (0.17 g, 0.62 mmol) and $PhNC(NH_2)NHPh$ (0.27 g, 1.3 mmol) yielded [MnBr{$PhNC(NH_2)NHPh$}$_2(CO)_3$] **6a**, as a yellow solid. Yield: 0.31 g (48%) (Found: C, 54.02; H, 4.41; N, 12.80. $C_{29}H_{26}BrMnN_6O_3$ requires C, 54.31; H, 4.09; N, 13.10%).

(*c*) The same reaction, as described in (*c*) above, using complex **1** (0.26 g, 0.95 mmol) and $PhNC(NH_2)NHPh$ (0.40 g, 1.9 mmol) gave [Mn{$PhNC(NH_2)NPh$}$(CO)_4$] **7a**, a yellow solid. Yield: 0.43 g (60%) (Found: C, 53.81; H, 3.53; N, 10.81. $C_{17}H_{12}MnN_3O_4$ requires C, 54.13, H, 3.21; N, 11.14%).

Complex 5b with triethylamine. Triethylamine (0.12 g, 0.5 mmol) was added to a solution of complex **5b** (0.25 g, 0.46 mmol) in diethyl ether–chloroform (2:1), and the mixture heated at 40 °C for 12 h. The reaction was monitored by IR spectroscopy in the carbonyl stretching region. The changes recorded were consistent with the formation of **6b** rather than of **7b**. Removal of the solvent *in vacuo* yielded a yellow solid which was recrystallised from hexane. Its IR spectrum was identical to that of **6b**.

Irradiation of complex 6b in hexane. The solution was exposed to sunlight, and the IR spectrum monitored over 2 d. New carbonyl absorptions slowly formed as the yellow solution became dark. After 2 d the solution was filtered through Celite and cooled to −20 °C for 2 d, after which time a yellow solid

separated. Infrared spectroscopy (Nujol) identified the product as complex **7b**: ν(CO) 2093m, 2010s, 1990s, 1933s; ν(NH) 3375w; ν(CN) 1601w cm^{-1}.

Complex 1 with lithio-*N*,*N*′,*N*″-triphenylguanidine in the presence of *N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethane (tmen). *n*-Butyllithium (2.3 mmol, 1.62 M in hexane) was added to a frozen solution of tmen (0.27 g, 2.3 mmol) in thf (5 cm^3) at −196 °C. The mixture was warmed to ambient temperature and stirred for 0.5 h before being cooled again to −196 °C. A solution of $PhNC(NHPh)_2$ (0.67 g, 2.3 mmol) in thf (20 cm^3) was added and the mixture warmed again to ambient temperature. After stirring for 0.75 h, a solution of complex **1** (0.64 g, 2.3 mmol) in thf (20 cm^3) was added dropwise to the lithioguanidine solution at −78 °C. After 2 h the reaction mixture was slowly warmed to room temperature before the solvent was removed *in vacuo* to yield a yellow gum. Extraction with diethyl ether, followed by evaporation, was found to be the most successful procedure for producing the solid product from the gum. Recrystallation from light petroleum (b.p. 60–80 °C) yielded **7b** as a yellow solid. Yield: 0.47 g (45% based on **1**) (Found: C, 61.68; H, 4.54; N, 8.56. $C_{23}H_{16}MnN_3O_4$ requires C, 60.94; H, 3.56; N, 9.27%). The same product was obtained from the same reactants in thf solution in the absence of tmen. Yield: 65%.

Complex 5b with *n*-butyllithium. The complex (0.24 g, 0.44 mmol), dissolved in monoglyme (ethylene glycol dimethyl ether) (15 cm^3), was cooled to −196 °C and *n*-butyllithium (0.43 mmol, 1.31 M in hexane) added. The mixture was allowed to warm to ambient temperature and stirred for 1.5 h. The solution darkened to deep orange-red. Removal of the solvent *in vacuo*, followed by extraction of the yellow residue into toluene (10 cm^3), produced a yellow solution, which after adjustment of the volume of solution *in vacuo*, addition of hexane and cooling to −10 °C yielded a small amount of a yellow solid, which IR spectroscopy showed to contain **6b** and not the target complex **7b**.

Tricarbonylchloro(η-cyclopentadienyl)molybdenum(II) 2 with *N*,*N*′,*N*″-triphenylguanidine. The guanidine (1.40 g, 4.9 mmol) in diethyl ether (10 cm^3) was added dropwise to a solution of complex **2** (0.68 g, 2.4 mmol) in diethyl ether (10 cm^3) at 35–40 °C, and the mixture heated at the reflux temperature for 1 h. After cooling and standing at room temperature, the solution was decanted from the white solid (*N*,*N*′,*N*″-triphenylguanidine hydrochloride), and filtered through a column of Celite 521. The red-wine coloured filtrate was evaporated to dryness *in vacuo*, and the red solid crystallised from a toluene–hexane mixture to yield dark red crystals of $[Mo(\eta\text{-}C_5H_5)\{PhNC(NHPh)NPh\}(CO)_2]$ **8b**. Yield: 0.91 g (75% based on **2**) (Found: C, 62.23; H, 4.31; Mo, 19.03; N, 8.16. $C_{26}H_{21}MoN_3O_2$ requires C, 62.03; H, 4.20; Mo, 19.06; N, 8.35%). ^1H NMR ($CDCl_3$): δ 5.53 (s, 5) and 6.91 (m, 15).

Complex 2 with *N*,*N*′-diphenylguanidine. Complex **2** (0.50 g, 1.8 mmol), dissolved in toluene (20 cm^3), was mixed with a solution of $PhNC(NH_2)NHPh$ (0.77 g, 3.7 mmol) in toluene (80 cm^3) and the red reaction mixture heated to 50 °C for 7 h. The solution remained clear but became orange-red. On cooling a white precipitate of $[(PhNH)_2CNH_2]Cl$ separated, and was filtered off. The filtrate was evaporated to dryness *in vacuo* until crystallisation was imminent, then the solution was cooled to −10 °C. Red-brown crystals of $[Mo(\eta\text{-}C_5H_5)\{PhNC(NH_2)NPh\}(CO)_2]$ **8a** formed, and were dried *in vacuo*. Yield: 0.59 g (78% based on **2**). M.p. 153 °C (decomp.) (Found: C, 56.13; H, 4.15; N, 9.86. $C_{20}H_{17}MoN_3O_2$ requires C, 56.22; H, 4.01; N, 9.83%). Mass spectrum: *m*/*z* 373, $[P - 2CO]^+$.

$[Mo(\eta\text{-}C_7H_7)(CO)_3]BF_4$ 9 with lithio-*N*,*N*′-di-*p*-tolylbenzamidine. A solution of the lithioamidine (0.67 mmol) in thf (15 cm^3) was transferred by syringe onto solid complex **9** (0.24 g, 0.67 mmol) at −40 °C. The mixture was allowed to warm and was stirred at ambient temperature for 2.5 h. Removal of the solvent *in vacuo* to small bulk (*ca.* 2 cm^3) and the addition of light petroleum (b.p. 60–80 °C, 30 cm^3) caused a white precipitate to separate. Filtration and cooling the solution to −10 °C gave a yellow solid which was filtered off. From the filtrate, cooling and addition of further light petroleum gave an orange-yellow solid of $[Mo\{\eta\text{-}C_7H_7(p\text{-}MeC_6H_4)NC(Ph)NC_6H_4Me\text{-}p\}(CO)_3]$ **10**. Yield: 0.16 g, 45% based on **9** (Found: C, 64.9; H, 4.69; N, 4.68. $C_{31}H_{26}MoN_2O_3$ requires C, 65.27; H, 4.59; N, 4.91%). IR (Nujol): ν(CO) 1925s, 1840s and 1800s cm^{-1}.

The corresponding *N*,*N*′-diphenylacetamidino complex was prepared by a similar procedure using monoglyme as the solvent. The product precipitated as a yellow solid during 24 h of stirring at ambient temperature (Found: C, 59.7; H, 4.30; N, 5.92. $C_{24}H_{20}MoN_2O_3$ requires C, 60.01; H, 4.20; N, 5.83%).

The same reaction using lithio-*N*,*N*′-di-*p*-tolylformamidine was also undertaken in monoglyme, but the product remained in solution. Removal of the solvent *in vacuo* at ambient temperature gave an orange gum, which was extracted with toluene. The solution changed from orange to black, and filtration through Celite 521 several times eventually gave an orange solution which yielded $[Mo(C_7H_8)(CO)_3]$ in low yield. This product was identified by analysis and IR spectroscopy, by reference to an authentic sample (Found: C, 44.2; H, 2.61. $C_{10}H_8MoO_3$ requires C, 44.1; H, 2.96%).

Complex 9 with lithio-*N*,*N*′-diphenylacetamidine in the presence of tmen. *N*,*N*′-Diphenylacetamidine (0.18 g, 0.9 mmol) and tmen (0.20 g, 1.7 mmol) were dissolved in monoglyme (20 cm^3), and the solution cooled to −196 °C. *n*-Butyllithium (0.9 mmol, 1.64 M in hexane) was added by syringe, and the mixture allowed to warm slowly to ambient temperature. After stirring for 1 h at this temperature the pale yellow solution was transferred by syringe onto complex **9** (0.30 g, 0.8 mmol), cooled to −196 °C. The reaction mixture was allowed to reach ambient temperature slowly, changing from yellow to yellow-orange and

Table 3 Crystal data for complexes **8a** and **8b**

	8a	**8b**
Formula	$C_{20}H_{17}MoN_3O_2$	$C_{26}H_{21}MoN_3O_2$
M	427.3	503.4
Colour	Brown	Brown
Crystal size/mm	0.3 × 0.35 × 0.45	0.07 × 0.3 × 0.4
T/K	150	150
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma* (no. 62)	$P2_1/c$ (no. 14)
a/Å	7.813(7)	10.935(1)
b/Å	18.565(8)	9.706(1)
c/Å	12.025(7)	21.483(2)
β/°		97.76(1)
U/Å³	1744(2)	2259.3(4)
Setting reflections, θ/°	24, 11–14	350, 10–20
Z	4	4
D_c/g cm^{-3}	1.63	1.48
μ/cm^{-1}	7.7	6.1
Maximum 2θ/°	50	60
Data total, unique, R_{int}	1722, 1585, 0.006	17 826, 6115, 0.086
Absorption correction	Empirical[a]	Semiempirical[b]
Minimum, maximum transmission	0.92, 1.00	0.80, 0.95
Data observed, $I > 2\sigma(I)$	1387	4066
Number of variables	128	373
$R(F$, observed data)	0.032	0.061
$wR(F^2$, all data)	0.081	0.135
Goodness of fit	1.15	1.17
Maximum, minimum Δρ/e Å^{-3}	0.47, −0.81	0.82, −0.99

[a] On 108 ψ scans of three reflections (TEXSAN software[34]). [b] On Laue equivalents (SHELXTL software).

finally dark amber. After 2 h of stirring at ambient temperature the solvent was removed *in vacuo* and the residue extracted with toluene (30 cm^3). Yellow-orange crystals of $[Mo(CO)_4(tmen)]$ separated from the yellow-orange solution on reducing the volume of solvent and cooling to −10 °C. Yield: 0.16 g (60% based on **9**) (Found: C, 37.11; H, 5.18; N, 8.17. $C_{10}H_{16}MoN_2O_4$ requires C, 37.05; H, 4.97; N, 8.64%). Infrared spectra and analytical data were consistent with data for an authentic sample prepared from $[Mo(CO)_6]$ and tmen.

Crystallography

X-Ray single-crystal diffraction experiments were performed for complex **8a** on a Rigaku AFC6S four-circle diffractometer (ω-scan mode with Lehmann–Larsen profile analysis) and for **8b** on a Siemens SMART three-circle diffractometer with a CCD area detector (full hemisphere of the reciprocal space scanned by ω in frames of 0.3°), using graphite-monochromated Mo-Kα radiation ($\bar{\lambda} = 0.710\ 73$ Å) and a Cryostream open-flow N_2 gas cryostat. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[33] The largest residual peaks of electron density were found at *ca.* 1 Å from the Mo atoms. Crystal data are given in Table 3.

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References

1 J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219.
2 T. Inglis, *Inorg. Chim. Acta Rev.*, 1973, **3**, 35.
3 D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.
4 N. de Vries, C. E. Costello, A. G. Jones and A. Davison, *Inorg. Chem.*, 1990, **29**, 1348.
5 R. Longhi and R. S. Drago, *Inorg. Chem.*, 1965, **4**, 11.
6 W. P. Fehlhammer, R. Metzner and W. Sperber, *Chem. Ber*, 1994, **127**, 829.
7 M. J. Begley, P. Hubberstey and P. H. Walton, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 502; *J. Chem. Soc.*, *Dalton Trans.*, 1995, 957; M. J. Begley, O. Eisenstein, P. Hubberstey, S. Jackson, C. E. Russell and P. H. Walton, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1935.
8 H.-K. Yip, C.-M. Che, Z.-Y. Zhou and T. C. W. Mak, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1369.
9 M. B. Dinger and W. Henderson, *Chem. Commun.*, 1996, 211.
10 (*a*) T. Inglis, M. Kilner, T. Reynoldson and E. E. Robertson, *J. Chem. Soc.*, *Dalton Trans.*, 1975, 924; (*b*) T. Inglis and M. Kilner, *ibid.*, 930; (*c*) B. Gaylani and M. Kilner, *J. Less-Common Met.*, 1977, **54**, 175; (*d*) B. Gaylani, M. Kilner, C. I. French, A. J. Pick and S. C. Wallwork, *Acta Crystallogr.*, *Sect. C*, 1991, **47**, 257.
11 R. J. Angelici and F. Basolo, *Inorg. Chem.*, 1963, **2**, 728 and refs. therein.
12 M. Kilner and A. Wojcicki, *Inorg. Chem.*, 1965, **4**, 591.
13 W. Heiber and M. Gscheidmeier, *Chem. Ber.*, 1966, **99**, 2312.
14 E. Lindner and K.-M. Matejcek, *J. Organomet. Chem.*, 1970, **24**, C57.
15 J. Locke and J. A. McCleverty, *Chem. Commun.*, 1965, 102.
16 R. J. Angelici, F. Basolo and A. J. Poe, *J. Am. Chem. Soc.*, 1963, **85**, 2215; C. C. Addison and M. Kilner, *J. Chem. Soc. A*, 1968, 1539.
17 F. A. Cotton, J. A. McCleverty, J. E. White, R. B. King, A. F. Fronzaglia and M. B. Bisnette, *Inorg. Synth.*, 1990, **28**, 45.
18 L. C. A. Carvalho, M. Dartiguenave and Y. Dartiguenave, *J. Organomet. Chem.*, 1989, **367**, 187.
19 P. L. Pauson, G. H. Smith and J. H. Valentine, *J. Chem. Soc. C*, 1967, 1061.
20 F. J. Hadley, T. M. Gilbert and R. D. Rodgers, *J. Organomet. Chem.*, 1993, **455**, 107.
21 E. E. Isaacs and W. A. G. Graham, *J. Organomet. Chem.*, 1975, **90**, 319.
22 A. Salzer, *Inorg. Chim. Acta*, 1976, **17**, 221.
23 P. Powell, M. Stephens and K. H. Yassin, *J. Organomet. Chem.*, 1986, **301**, 313.
24 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, Univ. Sci. Books, California, 1987.
25 Yu. F. Oprunenko, M. D. Reshetova, S. G. Malyugina, Yu. A. Ustynyuk, N. A. Ustynyuk, A. S. Batsanov, A. I. Yanovsky and Yu. T. Struchkov, *Organometallics*, 1994, **13**, 2284.
26 M. W. Creswick and I. Bernal, *Inorg. Chim. Acta*, 1983, **74**, 241; M. Draux and I. Bernal, *ibid.*, 1986, **114**, 75.
27 F. H. Allen, J. E. Davis, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J, M. Smith and D. G. Watson, *J. Chem. Inf. Comput. Sci.*, 1991, **31**, 187.
28 D. Fenske, E. Hartmann and K. Denicke, *Z. Naturforsch.*, *Teil B*, 1988, **43**, 1611; R. Gomez, R. Duchateau, A. N. Chernega, A. Meetsma, E. T. Edelmann, J. H. Teuben and M. L. H. Green, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 217.
29 Yu. V. Zefirov and P. M. Zorkii, *Russ. Chem. Rev.*, 1989, **58**, 421.
30 F. A. Cotton and R. Poli, *Inorg. Chim. Acta*, 1988, **141**, 91.
31 E. C. Taylor and W. A. Ehrhart, *J. Org. Chem.*, 1963, **28**, 1108.
32 R. B. King, *Organometallic Syntheses*, Wiley, New York, 1965.
33 G. M. Sheldrick, SHELXTL, Structure Determination Software Programs, Version 5/VMS, Siemens Analytical X-Ray Instruments, Madison, WI, 1995.
34 TEXSAN, Single Crystal Structure Analysis Software, Version 5.0, Molecular Structure Corporation, Houston, TX, 1989.

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