Journal of Organometallic Chemistry, 301 (1986) 109–130
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ASYMMETRICALLY BONDED π LIGANDS

I. HINGING AWAY FROM METAL OF SUBSTITUTED ALLYLS: SYNTHESES OF 1-*syn*-METHYL AND -PHENYL COMPLEXES, AND THE MOLECULAR STRUCTURES OF $[(\eta\text{-1-Ph-C}_3\text{H}_4)\text{Pd(tmeda)}]\text{BF}_4$, $[(\eta\text{-C}_5\text{H}_5)\text{Pd}(\eta\text{-1-Ph-C}_3\text{H}_4)]$, AND $[(\text{phen})\text{Mo(CO)}_2(\text{NCS})(\eta\text{-1-Ph-C}_3\text{H}_4)]$ AT 185 K

NICHOLAS W. MURRALL and ALAN J. WELCH*

Department of Chemistry, University of Edinburgh, Edinburgh, EH9 3JJ (Great Britain)

(Received July 24th, 1985)

Summary

Seven new complexes of (η-1-Me-C_3H_4) and (η-1-Ph-C_3H_4) with symmetric metal ligand backbones have been synthesised and spectroscopically characterised. Crystals of three of them, $[(\eta\text{-1-Ph-C}_3\text{H}_4)\text{Pd(tmeda)}]\text{BF}_4$ (**4**), $[(\eta\text{-C}_5\text{H}_5)\text{Pd}(\eta\text{-1-Ph-C}_3\text{H}_4)]$ (**5**), and $[(\text{phen})\text{Mo(CO)}_2(\text{NCS})(\eta\text{-1-Ph-C}_3\text{H}_4)]$ *(**8**), were suitable for X-ray diffraction studies. **4** is orthorhombic, $Pca2_1$, with four ion pairs in a cell of dimensions a 11.326(4), b 16.048(5), and c 9.950(3) Å. Using 4431 data measured at 185 K, R converged at 0.0311. Crystals of **5** are monoclinic, $P2_1/c$, with a 14.2255(19), b 5.8203(11), c 13.837(5) Å, and β 91.287(21°) at 185 K, $Z = 4$. 3064 amplitudes have been used to afford $R = 0.0267$. For **8** the monoclinic cell is a 15.658(4), b 9.473(3), c 15.666(6) Å, and β 113.95(3)°, $P2_1/a$, $Z = 4$. Low temperature (185 K) data were collected, and 3734 used to refine the structure to $R = 0.0362$.

The molecular structures of **4**, **5**, and **8** all reveal an η-1-*syn*-Ph-C_3H_4 ligand that is asymmetrically bonded to the metal atom, such that M–C(1) > M–C(3). Analysis of intra- and intermolecular contacts strongly suggests that, at least for **5**, the distortion in the metal–allyl bonding is electronic in origin.

Introduction

Of the very many organometallic reagents and intermediates that are of importance in modern organic chemistry [1] π-allyl transition metal complexes are of particular current interest [2,3]. Nucleophilic attack of a metal–allyl complex,

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* tmeda = *N,N,N′,N′*-tetramethylethylenediamine, phen = 1,10-phenanthroline.

0022-328X/86/$03.50

generating an alkene, is an extremely important chemical transformation, and here the stereochemistry of the product has been found to depend upon, amongst other things, the nature of additional ligands on the metal and any substituents present on the π-allyl function. Such findings have generated interest in the precise stereochemistries of π-allyl complexes, including the potentially asymmetric metal–allyl bonding that exists in complexes with either an asymmetric non-allyl ligand set, or in those with an asymmetrically substituted allyl.

There are a number of examples of the former type of complex. Classic representatives are $[(\eta\text{-2-Me-C}_3\text{H}_4)\text{Pd}(\text{PPh}_3)(\text{Cl})]$ [4] and $[(\eta\text{-2-Me-C}_3\text{H}_4)\overline{\text{Pd}\{\text{SC(Ph)C}}\text{(H)C(Ph)O}\}]$ [5], and in both the asymmetry in Pd–allyl bonding is readily understood in terms of the differing *trans* influences of the other ligating atoms.

There are considerably fewer examples of the latter type of complex, in spite of the quite reasonable assertion by Schwartz [6] that the electronic properties of the allyl termini in an asymmetrically substituted ligand may be quite different and lead to uneven bonding to a metal centre.

The first two papers in this series [7] are concerned with attempts to deliberately synthesise and structurally characterise complexes with asymmetrically substituted π-allyl ligands. In planning these studies a number of criteria have been applied:

(i) To observe and assess the effects of asymmetric substitution of an allyl ligand on its bonding to a transition metal it is clearly necessary to study complexes which are otherwise symmetric. Thus the allyl should be coordinated across a local mirror plane through an appropriate metal fragment (metal atom plus non-allyl ligands), and the allyl should not be additionally linked to any part of the molecule by a cyclic system.

(ii) Potential intramolecular interligand congestion should be avoided by the use of relatively compact ligands wherever possible.

(iii) Target complexes, once synthesised, should be studied by as accurate a crystallographic experiment as is feasible. This should at least involve a low temperature study, preferably with the recording of more than the minimum fraction of intensity data.

(iv) Since the area of most interest in the molecule is the metal coordination sphere, spurious electron density peaks and troughs in this region due to high X-ray absorption or its imperfect correction should be avoided at source by the non-use of third row transition metals and, for example, bromide or iodide ligands (assuming Mo-K_α X-radiation). This consideration, of course, further restricts the range of suitable target complexes.

(v) Assessment of the crystallographic results should take due account of the possibility of intermolecular interactions; if these are shown to be negligible then any unusual bonding features may be taken to arise from intramolecular effects with greater certainty.

(vi) Finally, any attempted interpretation of the electronic structure of the complex from its (crystallographically) determined molecular structure would be considerably reinforced if corroborative evidence could be found from a separate study in a different phase.

With these objectives, requirements, and limitations in mind we herein describe the syntheses of a number of 1-*syn*-methyl and 1-*syn*-phenyl substituted allyl complexes, and the determination of the crystal and molecular structures of three of the latter. A following paper will describe parallel studies of complexes with

1-*syn*-ethoxycarbonylallyl ligands, and our attempt to understand the electronic origins of the observed asymmetries in metal–allyl bonding by molecular orbital calculations at the extended Hückel level on model systems.

Experimental

Synthetic studies

All manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk tube techniques, and all solvents were dried and distilled under nitrogen and deoxygenated immediately prior to use. Commercially available reagents were used as supplied, whilst others were prepared by standard literature methods. ^1H NMR spectra were recorded on Brucker WP80SY, WP200SY, and WH360SY spectrometers, with chemical shifts referenced with respect to residual solvent protons relative to $SiMe_4$, positive values to high frequency. IR spectra were measured as either KBr discs or CH_2Cl_2 solutions on a Perkin–Elmer 598 spectrophotometer. Melting points were recorded in sealed, evacuated tubes on a Kofler hot stage microscope. Microanalyses were determined by the departmental service.

Bridge-cleavage reactions using $AgBF_4$

These reactions follow the method outlined by Schrock and Osborn [8].

*Synthesis of $[(\eta\text{-}1\text{-}Me\text{-}C_3H_4)Pd(cod)]BF_4$ * (1)*

To a solution of $[(\eta\text{-}1\text{-}Me\text{-}C_3H_4)PdCl]_2$ (0.197 g, 0.5 mmol) in CH_2Cl_2 (10 ml) was added solid $AgBF_4$ (0.19 g, 1 mmol). After stirring the mixture at room temperature for 5 min, cyclo-octa-1,5-diene (0.12 ml, ~ 1 mmol) was also added. After a further 1 min the solution was filtered and the residue washed with CH_2Cl_2 (2 × 5 ml). Addition of a large excess of Et_2O to the combined filtrate and washings afforded precipitation of $[(\eta\text{-}1\text{-}Me\text{-}C_3H_4)Pd(cod)]BF_4$ (**1**) as a white, microcrystalline solid. Recrystallisation by solvent diffusion (CH_2Cl_2/Et_2O 1/3 at $-30°C$) yielded diffraction-quality crystals; yield 0.29 g, 79%; (found: C, 40.0; H, 5.4. $C_{12}H_{19}BF_4Pd$ calcd.: C, 40.4; H, 5.4%); m.p. 168°C (dec.); ν_{max} (KBr disc) at 1950, 1890, 1485, 1453, 1433, 1380, 1298, 1050br, 883, 850, 820, 760, 735, 695, 668, and 524 cm^{-1}. ^1H NMR spectrum ($CDCl_3$, room temperature): δ 1.77 (d, 6.3 Hz, 3H, CH_3), 2.2–2.8 [m br, 8H, CH_2(cod)], 3.60 (d, 13.0 Hz, 1H, H(3a)), 4.67 (d, 6.6 Hz, 1H, H(3s)), 4.87 (d of t, 6.3, 12.6 Hz, 1H, H(1a)), 5.4–5.6 [m br, 1H, CH(cod)], 5.94 (d of d of d, 13.0, 12.6, 6.3 Hz, 1H, H(2s)), and 6.1–6.3 [m br, 3H, CH(cod)] ppm.

Synthesis of $[(\eta\text{-}1\text{-}Ph\text{-}C_3H_4)Pd(cod)]BF_4$ (2)

By an analogous method to that affording **1** was synthesised $[(\eta\text{-}1\text{-}Ph\text{-}C_3H_4)Pd(cod)]BF_4$ (**2**), as its ca. $0.5CH_2Cl_2$ solvate (as evidenced by microanalysis and NMR spectrum); white crystals; yield 0.30 g, 74%; (found: C, 46.6; H, 4.8. $C_{17}H_{21}BF_4Pd \cdot 0.5CH_2Cl_2$ calcd.: C, 45.6; H, 4.8%); m.p. 121°C; ν_{max} (KBr disc) at 3010, 2935, 2890, 1515, 1490, 1462, 1431, 1103, 1050br, 875, 757, and 686 cm^{-1}. ^1H NMR spectrum [$(CD_3)_2CO$, 193 K]: δ 2.2–2.8 [m br, 8H, CH_2 (cod)], 3.86 (d, 13.0 Hz, 1H, H(3a)), 4.4–4.5 [m br, 1H, CH (cod)], 5.05 (d, 7.3 Hz, 1H, H(3s)), 5.79 (d,

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* cod = cyclo-octa-1,5-diene.

12.6 Hz, 1H, H(1a)), 5.80 (s, 1H, $0.5CH_2Cl_2$), 6.3–6.4 [m br, 3H, CH (cod)], 6.94 (d of d of d, 7.3, 12.6, 13.0 Hz, 1H, H(2s)), and 7.4–7.9 (m, 5H, C_6H_5) ppm.

Synthesis of $[(\eta\text{-1-Me-}C_3H_4)Pd(tmeda)]BF_4$ *(3)*

The preparation of this complex has been reported previously [9]. In our hands an 85% yield was achieved. The complex was characterised by comparison of its ^1H NMR spectrum with that reported.

Synthesis of $[(\eta\text{-1-Ph-}C_3H_4)Pd(tmeda)]BF_4$ *(4)*

A similar procedure to that used above was employed to synthesise $[(\eta\text{-1-Ph-}C_3H_4)Pd(tmeda)]BF_4$ (**4**), as pale yellow crystals; yield 0.34 g, 80%; (found: C, 42.1; H, 5.7; N, 6.8. $C_{15}H_{25}BF_4N_2Pd$ calcd.: C, 42.2; H, 5.9; N, 6.6%); m.p. 164°C; ν_{max} (KBr disc) at 3010, 2965, 2910, 1490, 1465, 1285, 1050br, 950, 800, and 765 cm^{-1}. ^1H NMR spectrum [$(CD_3)_2CO$, room temperature]: δ 1.88 (s, 3H, MeN), 2.59 (s, 3H, MeN), 2.6–2.9 (m, 4H, CH_2CH_2), 2.87 (s, 3H, MeN), 3.06 (s, 3H, MeN), 3.36 (d of d of d, 12.3, < 1.0, < 1.0 Hz, 1H, H(3a)), 4.03 (d, 6.7 Hz, 1H, H(3s)), 4.64 (d, 11.8 Hz, 1H, H(1a)), 6.35 (d of d of d, 12.3, 11.8, 6.7 Hz, 1H, H(2s)), and 7.25–7.75 (m, 5H, C_6H_5) ppm.

Synthesis of $[(\eta\text{-}C_5H_5)Pd(\eta\text{-1-Ph-}C_3H_4)]$ *(5)*

Following the method of Robinson and Shaw [10], solutions in thf of $[(\eta\text{-1-Ph-}C_3H_4)PdCl]_2$ (0.25 g, 0.5 mmol) and $Na[C_5H_5]$ (5.0 ml, 0.2 *M*) were mixed. After stirring for 10 min the solvent was removed in vacuo and the red residue extracted with hexane (20 ml). Cooling to −30°C deposited red crystals of $[(\eta\text{-}C_5H_5)Pd(\eta\text{-1-Ph-}C_3H_4)]$ (**5**); yield 0.21 g, 73%; (found: C, 58.4; H, 5.1. $C_{14}H_{14}Pd$ calcd.: C, 58.2; H, 4.9%); m.p. 50°C; ν_{max} (KBr disc) at 3040, 3010, 2910, 2840, 1593, 1480, 1449sh, 1425, 1402, 1330, 1272, 1229, 1174, 1154sh, 1102, 1068, 1043, 1008, 979, 943, 918, 907, 863, 830, 806, 753, 691, 614, 590, 582, 528, and 436 cm^{-1}. ^1H NMR spectrum [$(CD_3)_2CO$, room temperature]: δ 2.35 (d of d, 10.6, 0.9 Hz, 1H, H(3a)), 3.60 (d, 6.1 Hz, 1H, H(3s)), 4.14 (d, 10.8 Hz, 1H, H(1a)), 5.55 (d of d of d, 10.8, 10.6, 6.1 Hz, 1H, H(2s)), 5.56 (s, 5H, C_5H_5), and 7.17–7.58 (m, 5H, C_6H_5) ppm.

Synthesis of $[(\eta\text{-}C_5H_5Mo(CO)_2(\eta\text{-1-Ph-}C_3H_4)]$ *(6)*

The synthesis of this complex follows the route established by Hayter [11]. Thus, a suspension of $Mo(CO)_6$, (1.31 g, 5 mmol) was refluxed in MeCN (20 ml) until it no longer sublimed out of solution (approx. 2 h). The resulting yellow solution was cooled to room temperature and cinnamylchloride (1.2 ml, 7.5 mmol) added. Refluxing the mixture for a further 18 h yielded a red solution which, upon removal of solvent in vacuo and washing with Et_2O (10 ml) afforded 1.8 g (92%) of crude $[Mo(CO)_2(MeCN)_2(Cl)(\eta\text{-1-Ph-}C_3H_4)]$. To a suspension of this (0.78 g, 2 mmol) in thf (20 ml) was added a freshly prepared solution of $Li[C_5H_5]$ in thf (10 ml, 0.2 *M*), and the mixture was stirred for 16 h at room temperature. The solution was concentrated to ca. 5 ml and loaded onto an alumina column (2.5 × 15 cm, Brockman Activity II). Elution with pentane afforded a yellow band. Removal of solvent in vacuo and slow evaporation of a 3/1 Et_2O/heptane solution yielded yellow crystals of $[(\eta\text{-}C_5H_5)Mo(CO)_2(\eta\text{-1-Ph-}C_3H_4)]$ (**6**); yield 0.49 g, 73%; (found: C, 57.3; H, 4.1. $C_{16}H_{14}MoO_2$ calcd.: C, 57.7; H, 4.2%); m.p. not recorded; ν_{max} (CO) (CH_2Cl_2 solution) at 1940 and 1862 cm^{-1}. ^1H NMR spectrum [$(CD_3)_2CO$, room temperature]: δ 0.9 (d br, 10 Hz, 1H, H(3a)), 2.48 (d, 10.4 Hz, 1H, H(1a)), 2.84 (d, 7.2 Hz, 1H, H(3s)), 5.13 (d of d of d, 10.0, 10.4, 7.2 Hz, 1H, H(2s)), 5.32 (s, 5H, C_5H_5), and 7.1–7.5 (m, 5H, C_6H_5) ppm.

Synthesis of complexes $[(L_2)Mo(CO)_2(NCS)(\eta\text{-}1\text{-}Ph\text{-}C_3H_4)]$

The experimental procedure has been established by Hull and Stiddard [12].

(a) L_2 = *bipy* *. To a solution of $[Mo(bipy)(CO)_4]$ (0.36 g, 1 mmol) in thf (20 ml) was added cinnamylchloride (2 ml) and the mixture refluxed for 2 h. The resulting brown precipitate of $[(bipy)Mo(CO)_2(Cl)(\eta\text{-}1\text{-}Ph\text{-}C_3H_4)]$ was filtered off and washed with thf (10 ml). To a suspension of it in Me_2CO was added KNCS (0.1 g, 1 mmol), and the mixture refluxed for 3 h. The resulting solution was filtered, added to H_2O (200 ml), and extracted with CH_2Cl_2 (4 × 50 ml). Extracts were dried over $MgSO_4$, the solvent removed under reduced pressure, and the residue recrystallised from CH_2Cl_2/hexane to afford purple microcrystals of $[(bipy)Mo(CO)_2(NCS)(\eta\text{-}1\text{-}Ph\text{-}C_3H_4)]$ (**7**); yield 0.37 g, 78%; (found: C, 54.4; H, 3.6; N, 8.9. $C_{22}H_{17}MoN_3O_2S$ calcd.: C, 54.7; H, 3.5; N, 8.7%); m.p. not recorded; ν_{max} (CH_2Cl_2 solution) at 2090 (NC), 1950 (CO), 1865 (CO), and 825 (CS) cm^{-1}. ^1H NMR spectrum $[(CD_3)_2CO$, room temperature]: δ 1.57 (d of d, 8.8, 1.9 Hz, 1H, H(1a)), 3.23 (d, 10.9 Hz, 1H, H(3a)), 3.43 (d of d, 6.6, 1.9 Hz, 1H, H(3s)), 4.14 (d of d of d, 6.6, 8.8, 10.9 Hz, 1H, H(2s)), 6.85–7.25 (m, 5H, C_6H_5), and 7.47–8.90 (m, 8H, bipy) ppm.

(b) L_2 = *phen.* Similarly, from $[Mo(phen)(CO)_6]$ was synthesised mauve crystals of $[(phen)Mo(CO)_2(NCS)(\eta\text{-}1\text{-}Ph\text{-}C_3H_4)]$ (**8**); yield 0.45 g, 89%; (found: C, 56.6; H, 3.7; N, 8.2. $C_{24}H_{17}MoN_3O_2S$ calcd.: C, 56.8; H, 3.3; N, 8.3%); m.p. not recorded; ν_{max} (CH_2Cl_2 solution) at 2087 (NC), 1949 (CO), 1864 (CO), and 845 (CS) cm^{-1}. ^1H NMR spectrum $[(CD_3)_2CO$, room temperature]: δ 1.68 (d of d, 9.0, 1.8 Hz, 1H, H(1a)), 3.30 (d, 10.2, 1H, H(3a)), 3.64 (d of d, 6.7, 1.8 Hz, 1H, H(3s)), 4.16 (d of d of d, 6.7, 9.0, 10.2 Hz, 1H, H(2s)), 7.2–7.5 (m, 5H, C_6H_5), and 7.8–9.9 (m, 8H, phen) ppm.

Preliminary crystallographic studies

Single crystals were either glued to a thin glass fibre, or sealed under N_2 inside a Lindemann capillary, using low temperature epoxy resin adhesive. Preliminary data were obtained using Cu-$K_{\bar{\alpha}}$ X-radiation and a Weissenberg goniometer.

(**1**) Orthorhombic, *a* 8.6, *b* 14.9, *c* 10.9 Å, *U* 1390 $Å^3$. D_x 1.64 g cm^{-3} for $Z = 4$. Space group $Cmc2_1$ (8-fold), *Cmc*2 ** (8-fold) or *Cmcm* (16-fold). Structure must be disordered.

(**2**) Poorly formed crystals which rapidly turn opaque at room temperature (solvent loss?). The use of alternative solvents afforded no improvement in crystal quality.

(**3**) Body-centred tetragonal lattice, *U* 780 $Å^3$. D_x 1.55 g cm^{-3} for $Z = 2$. Structure must be disordered.

(**4**) Primitive orthorhombic lattice, *U* 1810 $Å^3$. D_x 1.56 g cm^{-3} for $Z = 4$. Space group $Pca2_1$ (4-fold) or *Pcam* (8-fold). Data collection pursued.

(**5**) Primitive monoclinic lattice, *U* 1160 $Å^3$. D_x 1.67 g cm^{-3} for $Z = 4$. Space group $P2_1/c$ (4-fold). Data collection pursued.

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* bipy = 2,2′-bipyridyl.

** non-standard setting of *Ama*2.

(**6**) Very thin plates with poor optical properties (polarising microscope). Highly soluble in adhesive.
(**7**) Microcrystalline.
(**8**) Primitive monoclinic lattice. U 2200 Å^3. D_x 1.53 g cm^{-3} for $Z = 4$. Space group $P2_1/a$ * (4-fold). Data collection pursued.

Molecular structure determinations

All crystal data are at 185 ± 1 K.

[(η-1-Ph-C_3H_4)Pd(tmeda)]BF_4 ***(4)***

Crystal data. $C_{15}H_{25}BF_4N_2Pd$, $M = 426.5$. Orthorhombic, a 11.326(4), b 16.048(5), c 9.950(3) Å, U 1808.6 Å^3 (by least-squares refinement on 25 automatically centred diffractometer angles, $14.0° < \theta < 15.0°$, $\bar{\lambda}$ 0.71069 Å), space group $Pca2_1$ (C^5_{2v}, No. 29), $Z = 4$, D_x 1.566 g cm^{-3}, $F(000) = 864$, μ(Mo-K_α) 10.5 cm^{-1}.

Data collection and processing. CAD4 diffractometer with ULT1 low temperature attachment operating at 185 ± 1K, $\omega/2\theta$ mode with ω scan width 0.8 + 0.35 tanθ, variable scan rate dependent upon initial prescan, with only those reflections with $I \geqslant 0.5\sigma(I)$ rescanned such that final net intensity had $I > 50\sigma(I)$ subject to a maximum measuring time of 90 s. Graphite-monochromated Mo-K_α X-radiation. 5936 data measured, yielding 5206 unique data upon merging ($R_{merge} = 0.0633$). Data ranges $1.0° \leqslant \theta \leqslant 30.0°$ and $h,k,l \geqslant 0$; $h,k,l \leqslant 0$. 4431 data had $F_o \geqslant 2.0\sigma(F_o)$ and were retained. No crystal decay or movement over the data collection period (ca. 133 h). No absorption correction.

Structure analysis and refinement. Patterson synthesis (metal atom) followed by iterative full-matrix least-squares refinement and ΔF syntheses. Non-centrosymmetric space group suggested by E-statistics and confirmed by successful refinement, hence no disorder required. No distinction between alternative enantiomeric models could be made.

All non-H atoms allowed anisotropic thermal motion. Allylic hydrogen atoms located in a difference Fourier and thereafter positionally refined. Non-allylic hydrogens set in idealised positions, riding on their respective carbon atom, C–H 1.08 Å. All H atoms given fixed isotropic thermal parameter **, U 0.06 Å^2. Refinement with the weighting scheme $w^{-1} = [\sigma^2(F_o) + 0.01097F_o^2]$, in which $\sigma(F_o)$ is derived from counting statistics, converged at $R = 0.0311$, $R_w = 0.0554$, and $S = 0.6114$, for 231 variable parameters. No peak greater than 1.26 nor trough less than −1.25 e Å^{-3}. Table 1 lists coordinates of the atoms. Solution and refinement via SHELX76 [13] on the Edinburgh Regional Computer Centre ICL2972 machine using inlaid neutral scattering factors. For the metal, coefficients for an analytical approximation were taken from ref. 14. Molecular geometry calculations via XANADU [15], CALC [16], and XRAY76 [17]. Plotting via ORTEP-II [18] and SCHAKAL [19].

[(η-C_5H_5)Pd(η-1-Ph-C_3H_4)] ***(5)***

Crystal data. $C_{14}H_{14}Pd$, $M = 288.7$. Monoclinic, a 14.2255(19), b 5.8203(11), c 13.837(5) Å, β 91.287(21)°, U 1145.4 Å^3 (25 centred reflections, $15.0° < \theta < 16.0°$, $\bar{\lambda}$

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* Non-standard setting of $P2_1/c$.

** The isotropic temperature factor defined as $\exp\{-8\pi^2U(\sin^2\theta)/\lambda^2\}$.

TABLE 1

FRACTIONAL COORDINATES OF ATOMS WITH STANDARD DEVIATIONS FOR **4**

Atom	*x*	*y*	*z*
Pd	0.39985(2)	0.77262(1)	0.25000
C(1)	0.3467(3)	0.65017(22)	0.1792(4)
C(2)	0.2473(4)	0.70400(25)	0.1932(5)
C(3)	0.2463(4)	0.78092(25)	0.1281(5)
CR(1)	0.3612(3)	0.57353(18)	0.2578(5)
CR(2)	0.4341(4)	0.51048(25)	0.2084(4)
CR(3)	0.4476(4)	0.43501(25)	0.2771(4)
CR(4)	0.3879(4)	0.4225(3)	0.3988(5)
CR(5)	0.3183(5)	0.4854(3)	0.4487(5)
CR(6)	0.3033(4)	0.56025(25)	0.3801(4)
N(1)	0.4377(3)	0.90184(19)	0.2847(3)
N(2)	0.5682(3)	0.75170(24)	0.3413(3)
C(4)	0.5686(4)	0.9038(3)	0.3003(5)
C(5)	0.6081(4)	0.8354(3)	0.3930(6)
C(6)	0.4044(5)	0.9564(3)	0.1690(5)
C(7)	0.3774(4)	0.9340(3)	0.4051(4)
C(8)	0.6506(4)	0.7112(3)	0.2373(7)
C(9)	0.5677(4)	0.6921(3)	0.4548(5)
B	0.5136(4)	0.8227(3)	−0.1405(4)
F(1)	0.5657(4)	0.8121(3)	−0.2631(4)
F(2)	0.59580(21)	0.84708(25)	−0.0463(4)
F(3)	0.4256(3)	0.88201(17)	−0.1497(4)
F(4)	0.4646(3)	0.74759(20)	−0.1002(4)
H(12)	0.3912(20)	0.6593(20)	0.0937(22)
H(21)	0.1999(21)	0.6957(19)	0.2525(22)
H(31)	0.1972(21)	0.8229(19)	0.1613(21)
H(32)	0.2816(21)	0.7874(19)	0.0353(21)
HR(2)	0.4810	0.5201	0.1152
HR(3)	0.5036	0.3867	0.2366
HR(4)	0.3966	0.3644	0.4526
HR(5)	0.2739	0.4765	0.5437
HR(6)	0.2470	0.6081	0.4214
H(41)	0.6095	0.8953	0.2032
H(42)	0.5948	0.9632	0.3415
H(51)	0.7032	0.8361	0.3997
H(52)	0.5707	0.8458	0.4915
H(61)	0.4473	0.9343	0.0789
H(62)	0.4319	1.0196	0.1892
H(63)	0.3098	0.9547	0.1553
H(71)	0.3998	0.8958	0.4908
H(72)	0.2831	0.9324	0.3895
H(73)	0.4050	0.9974	0.4234
H(81)	0.6517	0.7642	0.1538
H(82)	0.6221	0.6606	0.2027
H(83)	0.7383	0.7163	0.2793
H(91)	0.5076	0.7139	0.5314
H(92)	0.6556	0.6874	0.4963
H(93)	0.5396	0.6317	0.4195

0.71069 Å), space group $P2_1/c$ (C_{2h}^5, No. 14), $Z = 4$, D_x 1.674 g cm^{-3}, $F(000) = 576$, μ(Mo-$K_{\bar{\alpha}}$) 15.4 cm^{-1}.

Data collection and processing. As for **4** except; 7541 data measured over ca. 144

h (no decay or crystal movement) in two quadrants ($h \pm k \pm l$) yielding 3331 unique data ($R_{\text{merge}} = 0.0169$) of which 3064 had $F_o \geqslant 2.0\sigma(F_o)$ and were retained; data were (non-analytically) corrected for absorption by a single ψ scan at $\chi = 90°$.

Structure analysis and refinement. As for **4** except: space group unambiguous; cyclopentadienyl ring showed rotational disorder, modelled in terms of two partial rings with site occupation factors of 0.54 and 0.46; cyclopentadienyl carbon atoms refined isotropically; $w^{-1} = [\sigma^2(F_o) + 0.000983F_o^2]$; R 0.0267, R_w 0.0453, S 0.9687 for 144 variables; greatest peak 0.62, deepest trough -0.57 e Å^{-3}; atomic coordinates appear in Table 2.

TABLE 2

FRACTIONAL COORDINATES OF ATOMS WITH STANDARD DEVIATIONS FOR 5

Atom	x	y	z
Pd	0.16303(1)	0.59064(2)	0.30294(1)
C(1)	0.22209(17)	0.4954(4)	0.16505(15)
C(2)	0.13038(20)	0.4091(4)	0.17720(19)
C(3)	0.05891(20)	0.5733(5)	0.19156(19)
CR(1)	0.30580(16)	0.3465(4)	0.16139(15)
CR(2)	0.38174(20)	0.4177(4)	0.10742(20)
CR(3)	0.46061(19)	0.2813(6)	0.09862(21)
CR(4)	0.46569(24)	0.0709(5)	0.1428(3)
CR(5)	0.39087(24)	−0.0030(5)	0.19767(22)
CR(6)	0.31151(23)	0.1350(5)	0.20730(20)
C(4)	0.1887(7)	0.8760(11)	0.4157(5)
C(5)	0.1096(4)	0.7376(14)	0.4460(4)
C(6)	0.1416(7)	0.5168(12)	0.4728(4)
C(7)	0.2377(6)	0.5064(14)	0.4531(4)
C(8)	0.2675(5)	0.7291(17)	0.4150(4)
C(4′)	0.1655(5)	0.8735(9)	0.4183(4)
C(5′)	0.1052(5)	0.6892(15)	0.4497(5)
C(6′)	0.1640(6)	0.4998(10)	0.4748(4)
C(7′)	0.2558(5)	0.5549(11)	0.4501(4)
C(8′)	0.2571(4)	0.7861(13)	0.4159(4)
H(12)	0.230(3)	0.649(8)	0.130(3)
H(21)	0.120(3)	0.237(7)	0.194(3)
H(31)	−0.000(3)	0.533(7)	0.216(3)
H(32)	0.057(3)	0.756(7)	0.150(3)
HR(2)	0.3792	0.5828	0.0718
HR(3)	0.5188	0.3409	0.0565
HR(4)	0.5270	−0.0364	0.1349
HR(5)	0.3944	−0.1680	0.2333
HR(6)	0.2542	0.0766	0.2508
H(41)	0.1874	1.0562	0.3972
H(51)	0.0374	0.7950	0.4478
H(61)	0.0998	0.3807	0.5029
H(71)	0.2825	0.3585	0.4643
H(81)	0.3370	0.7727	0.3909
H(41′)	0.1439	1.0463	0.4000
H(51′)	0.0294	0.6946	0.4535
H(61′)	0.1414	0.3409	0.5073
H(71′)	0.3157	0.4415	0.4559
H(81′)	0.3184	0.8781	0.3922

TABLE 3

FRACTIONAL COORDINATES OF ATOMS WITH STANDARD DEVIATIONS FOR **8**

Atom	x	y	z
Mo	0.30636(2)	0.48136(3)	0.75808(2)
N	0.26740(22)	0.6759(4)	0.67882(22)
C	0.2400(3)	0.7869(5)	0.6598(3)
S	0.19823(8)	0.94502(11)	0.62706(9)
N(1)	0.19621(21)	0.3833(3)	0.62913(20)
N(2)	0.16897(20)	0.5315(3)	0.76321(20)
C(4)	0.10701(25)	0.3926(4)	0.62320(24)
C(5)	0.2102(3)	0.3107(4)	0.5630(3)
C(6)	0.1387(3)	0.2408(4)	0.4901(3)
C(7)	0.0487(3)	0.2477(4)	0.4846(3)
C(8)	0.0310(3)	0.3285(4)	0.55141(25)
C(9)	−0.0610(3)	0.3506(4)	0.5475(3)
C(10)	−0.0759(3)	0.4342(4)	0.6093(3)
C(11)	0.00098(24)	0.4985(4)	0.68492(25)
C(12)	−0.0106(3)	0.5882(4)	0.7511(3)
C(13)	0.0659(3)	0.6481(4)	0.8191(3)
C(14)	0.1546(3)	0.6157(4)	0.8236(3)
C(15)	0.09192(24)	0.4754(4)	0.69226(24)
C(1)	0.3327(3)	0.3496(4)	0.8996(3)
C(2)	0.3028(3)	0.2680(4)	0.8187(3)
C(3)	0.3654(3)	0.2546(5)	0.7762(3)
CR(1)	0.2787(3)	0.3772(4)	0.9561(3)
CR(2)	0.3242(3)	0.4442(4)	1.0431(3)
CR(3)	0.2776(4)	0.4690(4)	1.1002(3)
CR(4)	0.1856(4)	0.4299(5)	1.0723(4)
CR(5)	0.1395(4)	0.3642(5)	0.9867(3)
CR(6)	0.1861(3)	0.3373(4)	0.9298(3)
CO(1)	0.4187(3)	0.4750(5)	0.7308(3)
CO(2)	0.3943(3)	0.5867(4)	0.8635(3)
O(1)	0.48563(23)	0.4756(4)	0.7175(3)
O(2)	0.44997(19)	0.6491(3)	0.92453(20)
H(12)	0.400(4)	0.356(5)	0.934(3)
H(21)	0.239(4)	0.245(5)	0.790(3)
H(31)	0.346(4)	0.205(5)	0.723(3)
H(32)	0.428(4)	0.260(5)	0.809(4)
H(51)	0.2801	0.3056	0.5659
H(61)	0.1539	0.1822	0.4388
H(71)	−0.0073	0.1923	0.4301
H(91)	−0.1197	0.2989	0.4937
H(101)	−0.1465	0.4534	0.6020
H(121)	−0.0796	0.6093	0.7479
H(131)	0.0580	0.7198	0.8691
H(141)	0.2146	0.6617	0.8792
HR(2)	0.3962	0.4766	1.0655
HR(3)	0.3137	0.5195	1.1671
HR(4)	0.1495	0.4502	1.1169
HR(5)	0.0672	0.3339	0.9643
HR(6)	0.1497	0.2844	0.8639

[(phen)Mo(CO)$_2$(NCS)(η-1-Ph-C$_3$H$_4$)] (8)

Crystal data. $C_{24}H_{17}MoN_3O_2S$, $M = 507.4$. Monoclinic, a 15.658(4), b 9.473(3), c 15.666(6) Å, β 113.95(3)°, U 2123.9 Å^3 (25 centred reflections, $12.0° < \theta < 13.0°$, λ 0.71069 Å), space group $P2_1/a$ (C^5_{2h}, No. 14), $Z = 4$, D_x 1.587 g cm^{-3}, $F(000) = 1024$, μ(Mo-K_α) 7.18 cm^{-1}.

Data collection and processing. As for **4** except: 8279 data measured over ca. 200 h (no decay or movement) in two quadrants ($h \pm k \pm l$), affording 3734 unique data ($R_{merge} = 0.0219$) of which 3014 were retained, $F_o > 2.0\sigma(F_o)$.

Structure analysis and refinement. As for **4** except; space group unambiguous; $w^{-1} = [\sigma^2(F_o) + 0.000545F_o^2]$; $R = 0.0362$, $R_w = 0.0399$, $S = 0.8699$ for 292 variables; greatest residue and deepest trough 0.43 and -0.45 e Å^{-3} respectively; atomic coordinates in Table 3.

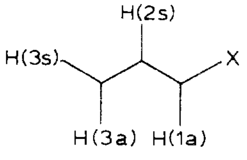
Results and discussion

Syntheses and characterisation

The new π-allyl complexes [(η-1-Me-C$_3$H$_4$)Pd(cod)]BF$_4$ (**1**), [(η-1-Ph-C$_3$H$_4$)Pd(cod)]BF$_4$ (**2**), [(η-1-Ph-C$_3$H$_4$)Pd(tmeda)]BF$_4$ (**4**), [(η-C$_5$H$_5$)Pd(η-1-Ph-C$_3$H$_4$)] (**5**), [(η-C$_5$H$_5$)Mo(CO)$_2$(η-1-Ph-C$_3$H$_4$)] (**6**), [(bipy)Mo(CO)$_2$(NCS)(η-1-Ph-C$_3$H$_4$)] (**7**) and [(phen)Mo(CO)$_2$(NCS)(η-1-Ph-C$_3$H$_4$)] (**8**) have been synthesised in > 70% yields by straightforward extensions of procedures outlined in ref. 8 (complexes **1** and **2**), ref. 9 (complex **4**), ref. 10 (complex **5**), ref. 11 (complex **6**) and ref. 12 (complexes **7** and **8**). In addition, [(η-1-Me-C$_3$H$_4$)Pd(tmeda)]BF$_4$ (**3**), was resynthesised [9] in an attempt to obtain diffraction-quality crystals.

Satisfactory elemental analyses (C, H and, where appropriate, N) were obtained for all new complexes. Some evidence for the η^3 nature of allyl coordination was furnished by the observation of absorptions in the IR spectra near 1450 cm^{-1} assigned to C=C stretching modes [20], but when Ph or (η-C$_5$H$_5$) functions are also present assignment becomes more tenuous [21]. IR bands due to the carbonyl groups of complexes **6**, **7** and **8** were clearly identified, as were those near 2090 and 830 cm^{-1} (complexes **7** and **8**) assigned to ν(NC) and ν(CS) respectively of an isothiocyanato function [22].

The most useful method of characterisation of these substituted allyl complexes was ^{1}H NMR spectroscopy, with spectra assigned (on the basis of coupling constants, chemical shifts, and by analogy) according to **9**, where X is the substituent



(**9**)

and a and s denote *anti* and *syn* positions relative to the unique proton H(2s). For all complexes, spectra were unequivocally interpreted in terms of 1-*syn*-substitution since this gives rise to two *trans* ^3J couplings (ca. 10–13 Hz) and only one *cis* ^3J coupling (ca. 7 Hz). H(3s) and H(2s) are readily assigned. In the methyl substituted complex **1** H(1a) is easily distinguished from H(3a) by the coupling of the former with methyl protons. For the phenyl substituted complexes the shielding effect of the substituent results in a shift to higher frequency of the resonance due to H(1a).

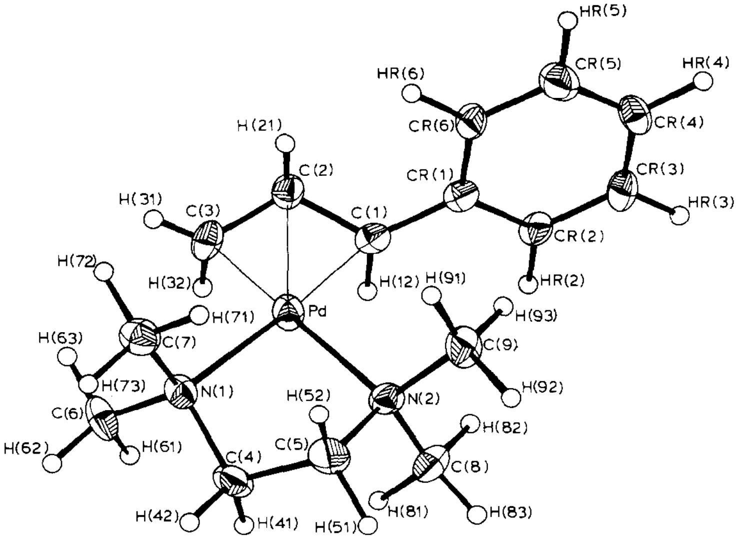


Fig. 1. Perspective view of the cation of [(η-1-Ph-C_3H_4)Pd(tmeda)]BF_4 (4).

Crystallographic results

Complexes **2**, **6** and **7** did not yield crystals of either sufficient size or quality for further study, and preliminary X-ray photographs of **1** and **3** showed that their crystal structures must be disordered.

Full diffraction data were recorded from the 1-phenyl substituted complexes **4**, **5** and **8**. Perspective views of single molecules [in the case of **4**, of the cation] are given

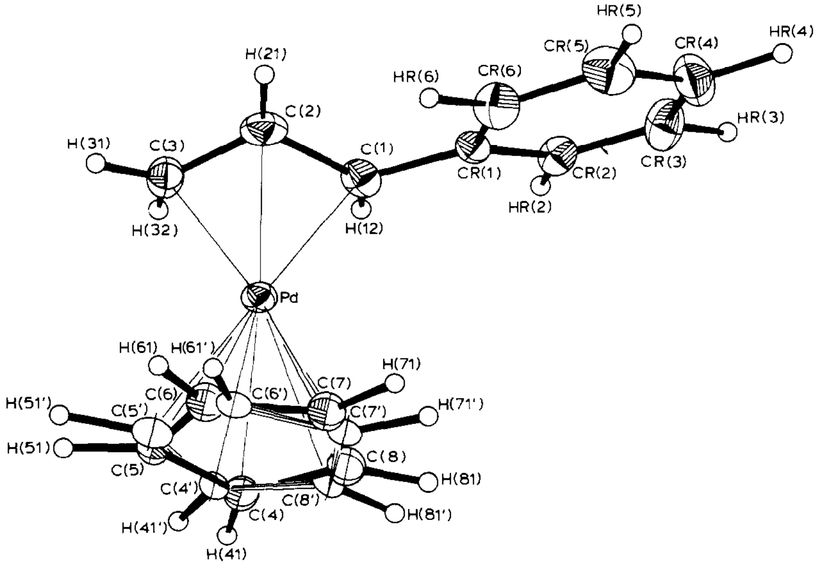


Fig. 2. Perspective view of [(η-C_5H_5)Pd(η-1-Ph-C_3H_4)] (5), showing both components of the disordered (η-C_5H_5) ligand.

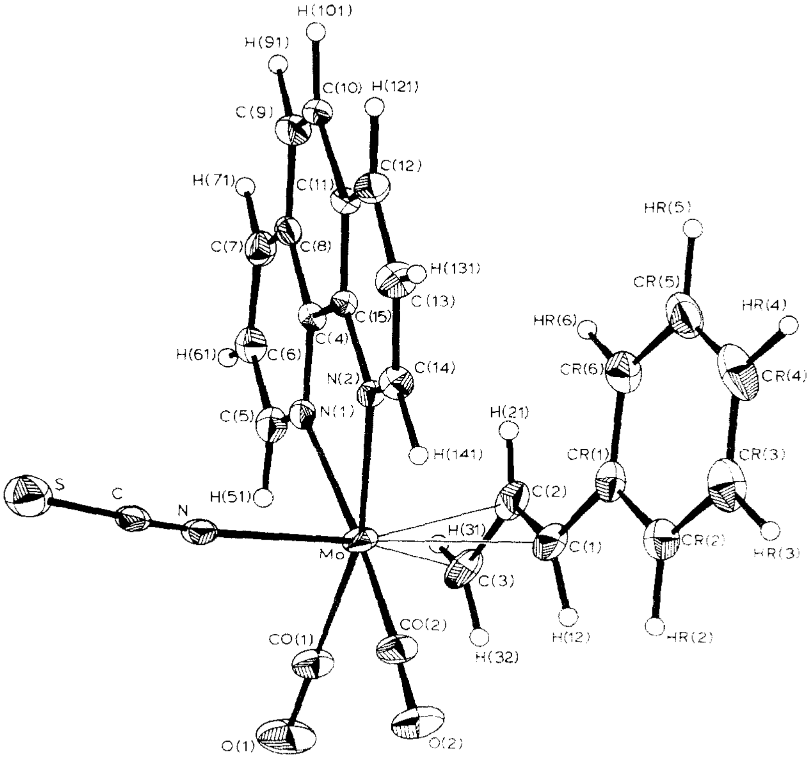


Fig. 3. Perspective view of [(phen)Mo(CO)$_2$(NCS)(η-1-Ph-C$_3$H$_4$)] (**8**).

in Figs. 1–3, respectively; a consistent numbering scheme is used throughout, in which allyl H atoms carry the number of the carbon to which they are bound followed by a number denoting position, 1 for *syn*, 2 for *anti*. Phenyl rings are numbered cyclically, with CR(2) *anti* to C(2). Tables 4–6 list selected interatomic distances and interbond angles, whilst Tables 7–9 (deposited) carry details of various best (least-squares) planes calculations on **4**, **5** and **8**, respectively.

Non-allyl ligands. In **4** the 5-membered PdNCCN ring adopts an approximate skew conformation in the crystal, with the C–C bond roughly parallel to C(2)–C(3) of the allyl ligand. The P–N bond lengths are neither significantly different from each other or from those in the parent species [(η-C$_3$H$_5$)Pd(tmeda)]$^+$ [9], and there is reasonable correlation between the Pd–N distances and N–Pd–N angle in **4** in comparison with other tmeda complexes [23–25]. Although the distances Pd–N(1) and Pd–N(2) are not statistically different, it is of some interest to note that the longer, Pd–N(1), is *trans* to the longest Pd–C bond, Pd–C(1). This is in marked contrast to the relative Ir–P bond lengths in [(η-1-Ph-C$_3$H$_4$)Ir(PPh$_3$)$_2$(H)Cl] (**10**) [26]. However, PPh$_3$ is a σ-donor, π-acceptor ligand whereas tmeda is a pure σ-donor and thus not necessarily susceptible [27] to the *trans* influence of π-bonded functions such as allyls.

In **5** the (η-C$_5$H$_5$) ligand is rotationally disordered about the metal–ligand axis over two sites whose occupation factors are 0.54 and 0.46. Atoms of the minor component carry prime superscripts in Fig. 2. The two C$_5$ rings are inclined at an

TABLE 4

INTER-ATOMIC DISTANCES (Å) AND INTER-BOND ANGLES (°) FOR **4**

Pd-C(1)	2.173(3)	CR(5)-CR(6)	1.392(6)
Pd-C(2)	2.125(4)	N(1)-C(4)	1.492(6)
Pd-C(3)	2.124(5)	N(1)-C(6)	1.495(6)
Pd-N(1)	2.146(3)	N(1)-C(7)	1.472(5)
Pd-N(2)	2.138(3)	N(2)-C(5)	1.508(6)
C(1)-C(2)	1.425(5)	N(2)-C(8)	1.478(6)
C(1)-CR(1)	1.467(5)	N(2)-C(9)	1.479(6)
C(2)-C(3)	1.394(6)	C(4)-C(5)	1.501(7)
CR(1)-CR(2)	1.395(6)	B-F(1)	1.366(6)
CR(1)-CR(6)	1.398(6)	B-F(2)	1.378(5)
CR(2)-CR(3)	1.399(6)	B-F(3)	1.380(5)
CR(3)-CR(4)	1.401(6)	B-F(4)	1.387(6)
CR(4)-CR(5)	1.374(7)		
C(1)-H(12)	1.00(3)	C(3)-H(31)	0.93(3)
C(2)-H(21)	0.81(3)	C(3)-H(32)	1.01(3)
C(1)-Pd-C(2)	38.72(15)	CR(4)-CR(5)-CR(6)	121.8(4)
C(1)-Pd-C(3)	69.18(15)	CR(1)-CR(6)-CR(5)	120.1(4)
C(1)-Pd-N(1)	169.03(13)	Pd-N(1)-C(4)	103.61(25)
C(1)-Pd-N(2)	104.06(13)	Pd-N(1)-C(6)	113.1(3)
C(2)-Pd-C(3)	38.29(17)	Pd-N(1)-C(7)	112.19(25)
C(2)-Pd-N(1)	134.90(14)	C(4)-N(1)-C(6)	108.6(3)
C(2)-Pd-N(2)	139.15(15)	C(4)-N(1)-C(7)	111.7(3)
C(3)-Pd-N(1)	101.23(15)	C(6)-N(1)-C(7)	107.7(3)
C(3)-Pd-N(2)	169.18(15)	Pd-N(2)-C(5)	105.8(3)
N(1)-Pd-N(2)	84.57(13)	Pd-N(2)-C(8)	108.5(3)
Pd-C(1)-C(2)	68.84(22)	Pd-N(2)-C(9)	115.0(3)
Pd-C(1)-CR(1)	123.7(3)	C(5)-N(2)-C(8)	110.2(4)
C(2)-C(1)-CR(1)	123.0(3)	C(5)-N(2)-C(9)	108.4(3)
Pd-C(2)-C(1)	72.44(22)	C(8)-N(2)-C(9)	108.8(4)
Pd-C(2)-C(3)	70.8(3)	N(1)-C(4)-C(5)	110.2(4)
C(1)-C(2)-C(3)	119.9(4)	N(2)-C(5)-C(4)	110.6(4)
Pd-C(3)-C(2)	70.9(3)	F(1)-B-F(2)	110.6(4)
C(1)-CR(1)-CR(2)	119.1(3)	F(1)-B-F(3)	109.8(4)
C(1)-CR(1)-CR(6)	122.6(3)	F(1)-B-F(4)	108.9(4)
CR(2)-CR(1)-CR(6)	118.2(4)	F(2)-B-F(3)	109.7(4)
CR(1)-CR(2)-CR(3)	121.4(4)	F(2)-B-F(4)	108.6(4)
CR(2)-CR(3)-CR(4)	119.6(4)	F(3)-B-F(4)	109.3(4)
CR(3)-CR(4)-CR(5)	118.9(4)		
Pd-C(1)-H(12)	90.2(15)	Pd-C(3)-H(31)	109.4(16)
H(12)-C(1)-C(2)	113.1(15)	Pd-C(3)-H(32)	101.8(15)
H(12)-C(1)-CR(1)	121.4(15)	C(2)-C(3)-H(31)	118.7(16)
Pd-C(2)-H(21)	115.6(18)	C(2)-C(3)-H(32)	120.8(15)
C(1)-C(2)-H(21)	119.7(19)	H(31)-C(3)-H(32)	118.9(22)
H(21)-C(2)-C(3)	118.6(19)		

angle of 3.9° to each other and subtend angles of 20.4° (major component) and 22.2° (minor) to the allyl C_3 plane, values that compare favourably with that (20.0°) determined in $[(\eta\text{-}C_5H_5)Pd(\eta\text{-}C_3H_5)]$ [28]. Both $(\eta\text{-}C_5H_5)$ rings in **5** are asymmetrically bonded to the metal atom which is slipped across the 5-atom face, in a

TABLE 5

INTER-ATOMIC DISTANCES (Å) AND INTER-BOND ANGLES (°) FOR **5**

Pd–C(1)	2.1739(23)	CR(1)–CR(2)	1.390(4)
Pd–C(2)	2.079(3)	CR(1)–CR(6)	1.387(4)
Pd–C(3)	2.116(3)	CR(2)–CR(3)	1.382(4)
Pd–C(4)	2.302(8)	CR(3)–CR(4)	1.370(5)
Pd–C(5)	2.302(7)	CR(4)–CR(5)	1.389(5)
Pd–C(6)	2.415(8)	CR(5)–CR(6)	1.394(4)
Pd–C(7)	2.364(8)	C(4)–C(5)	1.454(10)
Pd–C(8)	2.272(8)	C(4)–C(8)	1.410(11)
Pd–C(4′)	2.292(6)	C(5)–C(6)	1.411(10)
Pd–C(5′)	2.282(8)	C(6)–C(7)	1.401(11)
Pd–C(6′)	2.436(7)	C(7)–C(8)	1.466(11)
Pd–C(7′)	2.410(6)	C(4′)–C(5′)	1.446(10)
Pd–C(8′)	2.332(6)	C(4′)–C(8′)	1.400(9)
C(1)–C(2)	1.412(4)	C(5′)–C(6′)	1.422(10)
C(1)–CR(1)	1.475(3)	C(6′)–C(7′)	1.395(9)
C(2)–C(3)	1.413(4)	C(7′)–C(8′)	1.427(9)
C(1)–H(12)	1.02(5)	C(3)–H(31)	0.94(5)
C(2)–H(21)	1.04(4)	C(3)–H(32)	1.21(4)
C(1)–Pd–C(2)	38.69(10)	C(5′)–Pd–C(8′)	59.58(24)
C(1)–Pd–C(3)	68.07(10)	C(6′)–Pd–C(7′)	33.45(22)
C(1)–Pd–C(4)	136.07(21)	C(6′)–Pd–C(8′)	57.39(22)
C(1)–Pd–C(5)	172.50(18)	C(7′)–Pd–C(8′)	34.98(21)
C(1)–Pd–C(6)	150.27(19)	Pd–C(1)–C(2)	67.03(14)
C(1)–Pd–C(7)	122.95(19)	Pd–C(1)–CR(1)	120.55(16)
C(1)–Pd–C(8)	115.45(20)	C(2)–C(1)–CR(1)	122.97(21)
C(1)–Pd–C(4′)	142.55(16)	Pd–C(2)–C(1)	74.28(15)
C(1)–Pd–C(5′)	178.36(20)	Pd–C(2)–C(3)	71.73(16)
C(1)–Pd–C(6′)	143.88(17)	C(1)–C(2)–C(3)	116.49(23)
C(1)–Pd–C(7′)	120.30(16)	Pd–C(3)–C(2)	68.93(15)
C(1)–Pd–C(8′)	119.04(16)	C(1)–CR(1)–CR(2)	118.75(21)
C(2)–Pd–C(3)	39.34(11)	C(1)–CR(1)–CR(6)	123.02(22)
C(2)–Pd–C(4)	164.31(21)	CR(2)–CR(1)–CR(6)	118.20(23)
C(2)–Pd–C(5)	146.80(19)	CR(1)–CR(2)–CR(3)	121.21(25)
C(2)–Pd–C(6)	133.88(20)	CR(2)–CR(3)–CR(4)	120.6(3)
C(2)–Pd–C(7)	135.87(20)	CR(3)–CR(4)–CR(5)	119.2(3)
C(2)–Pd–C(8)	151.88(21)	CR(4)–CR(5)–CR(6)	120.4(3)
C(2)–Pd–C(4′)	161.28(17)	CR(1)–CR(6)–CR(5)	120.4(3)
C(2)–Pd–C(5′)	142.60(20)	Pd–C(4)–C(5)	71.6(4)
C(2)–Pd–C(6′)	134.65(18)	Pd–C(4)–C(8)	70.9(4)
C(2)–Pd–C(7′)	140.43(17)	C(5)–C(4)–C(8)	106.7(7)
C(2)–Pd–C(8′)	157.38(17)	Pd–C(5)–C(4)	71.6(4)
C(3)–Pd–C(4)	128.75(21)	Pd–C(5)–C(6)	77.1(4)
C(3)–Pd–C(5)	113.88(19)	C(4)–C(5)–C(6)	109.4(6)
C(3)–Pd–C(6)	126.79(20)	Pd–C(6)–C(5)	68.2(4)
C(3)–Pd–C(7)	157.49(20)	Pd–C(6)–C(7)	71.0(4)
C(3)–Pd–C(8)	161.96(21)	C(5)–C(6)–C(7)	107.4(7)
C(3)–Pd–C(4′)	122.75(17)	Pd–C(7)–C(6)	75.0(4)
C(3)–Pd–C(5′)	113.56(20)	Pd–C(7)–C(8)	68.2(4)
C(3)–Pd–C(6′)	133.56(18)	C(6)–C(7)–C(8)	108.9(7)
C(3)–Pd–C(7′)	166.45(17)	Pd–C(8)–C(4)	73.2(5)
C(3)–Pd–C(8′)	153.34(17)	Pd–C(8)–C(7)	75.0(4)
C(4)–Pd–C(5)	36.8(3)	C(4)–C(8)–C(7)	107.3(7)

TABLE 5 (continued)

C(4)–Pd–C(6)	59.4(3)	Pd–C(4′)–C(5′)	71.2(4)
C(4)–Pd–C(7)	59.5(3)	Pd–C(4′)–C(8′)	73.9(4)
C(4)–Pd–C(8)	35.9(3)	C(5′)–C(4′)–C(8′)	107.3(6)
C(5)–Pd–C(6)	34.7(3)	Pd–C(5′)–C(4′)	72.0(4)
C(5)–Pd–C(7)	58.10(25)	Pd–C(5′)–C(6′)	78.5(4)
C(5)–Pd–C(8)	60.3(3)	C(4′)–C(5′)–C(6′)	107.4(6)
C(6)–Pd–C(7)	34.1(3)	Pd–C(6′)–C(5′)	66.6(4)
C(6)–Pd–C(8)	59.6(3)	Pd–C(6′)–C(7′)	72.3(4)
C(7)–Pd–C(8)	36.8(3)	C(5′)–C(6′)–C(7′)	108.1(6)
C(4′)–Pd–C(5′)	36.87(24)	Pd–C(7′)–C(6′)	74.3(4)
C(4′)–Pd–C(6′)	58.44(22)	Pd–C(7′)–C(8′)	69.5(3)
C(4′)–Pd–C(7′)	58.29(21)	C(6′)–C(7′)–C(8′)	108.5(6)
C(4′)–Pd–C(8′)	35.24(21)	Pd–C(8′)–C(4′)	70.9(3)
C(5′)–Pd–C(6′)	34.89(25)	Pd–C(8′)–C(7′)	75.5(4)
C(5′)–Pd–C(7′)	58.08(24)	C(4′)–C(8′)–C(7′)	108.3(5)
Pd–C(1)–H(12)	103.9(25)	Pd–C(3)–H(31)	111.8(28)
H(12)–C(1)–C(2)	118.8(26)	Pd–C(3)–H(32)	108.1(20)
H(12)–C(1)–CR(1)	113.4(26)	C(2)–C(3)–H(31)	122.3(28)
Pd–C(2)–H(21)	109.8(24)	C(2)–C(3)–H(32)	122.1(20)
C(1)–C(2)–H(21)	120.4(24)	H(31)–C(3)–H(32)	112.4(34)
H(21)–C(2)–C(3)	121.0(24)		

direction roughly away from C(6)–C(7) or C(6′)–C(7′), by ca. 0.13 and 0.16 Å respectively. In so doing the palladium atom tends towards a 16e configuration with *trans* allyl functions analogous to those in $[(\eta\text{-}C_3H_5)_2Pd]$ [29], with concomitant partial C–C localisation in the C(6)–C(7) and C(6′)–C(7′) bonds. Many other examples of $(\eta\text{-}C_5H_5)$ asymmetrically bonded to palladium are known [30–34].

The overall arrangement of ligands in **8** is the same as that in $[(\text{bipy})\text{Mo(CO)}_2(\text{NCS})(\eta\text{-}C_3H_5)]$ (**11**) [35], (bipy = 2,2′-bipyridyl), $[(\text{phen})\text{Mo(CO)}_2(\text{NCS})(\eta\text{-2-Me-}C_3H_4)]$, (**12**) [36], $[(\text{bipy})\text{Mo(CO)}_2(\text{py})(\eta\text{-}C_5H_5)]^+$ (**13**) [37], (py = pyridyl), and other members of the series $[L_2\text{Mo(CO)}_2(L')(\text{allyl})]$ in which L_2 is not a strongly π-accepting ligand [38–40], in that L_2 lies *trans* to the carbonyl groups. With respect to the Mo(CO)_2 unit the conformation of the allyl function in **8** is *exo*, consistent with the solid state structures of **11**–**13** and numerous other formally 7-coordinate species containing the $[\text{Mo(CO)}_2(\text{allyl})]$ moiety [38–47]. With respect to corresponding parameters within this family of complexes, the Mo–CO lengths and the OC–Mo–CO angle in **8** are quite normal. Similarly, the Mo–N(1) and Mo–N(2) distances in (**8**), mean 2.246 Å, correlate well with the N(1)–Mo–N(2) angle, 70.90(11)°, in an analogous way to that established for other phenanthroline complexes [48]. There are, moreover, no significant differences between parameters within the coordinated phen ligand of **8** and corresponding ones of the free molecule [49]. The Mo–NCS bond length in **8** is, however, significantly longer than that in **11** and **12**, and is complemented by a rather short N–C bond and somewhat bent Mo–N–CS angle.

The η-1-syn-phenylallyl ligands. The present crystallographic studies of **4**, **5** and **8**, taken together with the previous determination [26] of **10**, afford accurate molecular structures of, respectively, 4-, 5-, 7- and 6-coordinate complexes of the η-1-*syn*-Ph-C_3H_4 ligand with an otherwise symmetric backbone. For comparative

TABLE 6

INTER-ATOMIC DISTANCES (Å) AND INTER-BOND ANGLES (°) FOR **8**

Mo–N	2.167(3)	C(8)–C(9)	1.433(6)
Mo–N(1)	2.256(3)	C(9)–C(10)	1.341(6)
Mo–N(2)	2.236(3)	C(10)–C(11)	1.437(5)
Mo–C(1)	2.429(4)	C(11)–C(12)	1.408(6)
Mo–C(2)	2.243(4)	C(11)–C(15)	1.399(5)
Mo–C(3)	2.311(5)	C(12)–C(13)	1.362(6)
Mo–CO(1)	1.972(5)	C(13)–C(14)	1.396(6)
Mo–CO(2)	1.943(4)	C(1)–C(2)	1.393(6)
N–C	1.128(5)	C(1)–CR(1)	1.475(6)
C–S	1.632(5)	C(2)–C(3)	1.398(6)
N(1)–C(4)	1.365(5)	CR(1)–CR(2)	1.407(6)
N(1)–C(5)	1.333(5)	CR(1)–CR(6)	1.389(6)
N(2)–C(14)	1.325(5)	CR(2)–CR(3)	1.386(7)
N(2)–C(15)	1.373(5)	CR(3)–CR(4)	1.375(7)
C(4)–C(8)	1.401(5)	CR(4)–CR(5)	1.386(7)
C(4)–C(15)	1.431(5)	CR(5)–CR(6)	1.384(7)
C(5)–C(6)	1.398(6)	CO(1)–O(1)	1.149(6)
C(6)–C(7)	1.377(6)	CO(2)–O(2)	1.160(5)
C(7)–C(8)	1.412(6)		
C(1)–H(12)	0.98(5)	C(3)–H(31)	0.89(5)
C(2)–H(21)	0.93(5)	C(3)–H(32)	0.91(6)
N–Mo–N(1)	84.37(12)	N(1)–C(4)–C(15)	117.5(3)
N–Mo–N(2)	77.80(12)	C(8)–C(4)–C(15)	119.8(3)
N–Mo–C(1)	149.77(14)	N(1)–C(5)–C(6)	123.4(4)
N–Mo–C(2)	163.57(14)	C(5)–C(6)–C(7)	119.1(4)
N–Mo–C(3)	150.07(15)	C(6)–C(7)–C(8)	118.9(4)
N–Mo–CO(1)	88.29(16)	C(4)–C(8)–C(7)	118.1(4)
N–Mo–CO(2)	89.29(15)	C(4)–C(8)–C(9)	118.9(4)
N(1)–Mo–N(2)	73.90(11)	C(7)–C(8)–C(9)	123.0(4)
N(1)–Mo–C(1)	112.98(13)	C(8)–C(9)–C(10)	121.4(4)
N(1)–Mo–C(2)	82.34(14)	C(9)–C(10)–C(11)	120.8(4)
N(1)–Mo–C(3)	81.34(14)	C(10)–C(11)–C(12)	123.2(4)
N(1)–Mo–CO(1)	102.58(15)	C(10)–C(11)–C(15)	119.0(3)
N(1)–Mo–CO(2)	173.33(15)	C(12)–C(11)–C(15)	117.7(3)
N(2)–Mo–C(1)	83.44(13)	C(11)–C(12)–C(13)	119.5(4)
N(2)–Mo–C(2)	89.22(14)	C(12)–C(13)–C(14)	119.2(4)
N(2)–Mo–C(3)	122.43(14)	C(2)–C(14)–C(13)	123.4(4)
N(2)–Mo–CO(1)	165.88(15)	N(2)–C(15)–C(4)	117.6(3)
N(2)–Mo–CO(2)	102.74(15)	N(2)–C(15)–C(11)	122.5(3)
C(1)–Mo–C(2)	34.40(15)	C(4)–C(15)–C(11)	119.9(3)
C(1)–Mo–C(3)	59.94(16)	Mo–C(1)–C(2)	65.47(24)
C(1)–Mo–CO(1)	110.26(17)	Mo–C(1)–CR(1)	122.0(3)
C(1)–Mo–CO(2)	71.89(16)	C(2)–C(1)–CR(1)	125.6(4)
C(2)–Mo–C(3)	35.71(16)	Mo–C(2)–C(1)	80.1(3)
C(2)–Mo–CO(1)	104.00(17)	Mo–C(2)–C(3)	74.8(3)
C(2)–Mo–CO(2)	103.54(17)	C(1)–C(2)–C(3)	116.2(4)
C(3)–Mo–CO(1)	69.52(18)	Mo–C(3)–C(2)	69.5(3)
C(3)–Mo–CO(2)	105.26(17)	C(1)–CR(1)–CR(2)	118.2(4)
CO(1)–Mo–CO(2)	79.26(18)	C(1)–CR(1)–CR(6)	123.9(4)
Mo–N–C	158.7(3)	CR(2)–CR(1)–CR(6)	117.9(4)
N–C–S	177.2(4)	CR(1)–CR(2)–CR(3)	120.6(4)
Mo–N(1)–C(4)	115.07(24)	CR(2)–CR(3)–CR(4)	120.5(5)

TABLE 6 (continued)

Mo-N(1)-C(5)	127.0(3)	CR(3)-CR(4)-CR(5)	119.7(5)
C(4)-N(1)-C(5)	117.7(3)	CR(4)-CR(5)-CR(6)	120.1(5)
Mo-N(2)-C(14)	126.8(3)	CR(1)-CR(6)-CR(5)	121.2(4)
Mo-N(2)-C(15)	115.50(23)	Mo-CO(1)-O(1)	177.2(4)
C(14)-N(2)-C(15)	117.6(3)	Mo-CO(2)-O(2)	176.7(4)
N(1)-C(4)-C(8)	122.6(3)		
Mo-C(1)-H(12)	102.6(31)	Mo-C(3)-H(32)	107.2(35)
H(12)-C(1)-C(2)	115.4(32)	C(2)-C(3)-H(31)	116.9(35)
H(12)-C(1)-CR(1)	114.4(32)	C(2)-C(3)-H(32)	122.2(35)
Mo-C(2)-H(21)	101.9(34)	H(31)-C(3)-H(32)	116.3(50)
C(1)-C(2)-H(21)	117.2(34)		
H(21)-C(2)-C(3)	124.8(34)		
Mo-C(3)-H(31)	113.8(35)		

purposes the atomic numbering in **10** has been modified for consistency with that of **4**, **5** and **8**.

In the context of our interest in asymmetric metal–allyl bonding the key feature common to all these species is that the allylic carbon bearing the phenyl substituent, C(1), is significantly further from the metal than is the other terminal carbon, C(3).

A single parameter, β, the angle between the vector M–O (M is the metal atom, O is the centre of mass of the allyl C_3 fragment) and a vector parallel to $C(1) \cdots C(3)$ passing through O, has been used [50] by Ibers et al. to define this asymmetric bonding. The sense of β is chosen such that when $\beta < 90°$ the substituted carbon is hinged away from the metal atom. Table 10 lists β, together with other important parameters relating to the coordinated η-1-Ph-C_3H_4 ligand, of **4**, **5**, **10** and **8**. With the exception of **8**, a complex in which there is extensive intramolecular interligand crowding, all complexes have β between 88 and 89°.

Another important quantity is τ, the angle by which the allyl central carbon, C(2), is tilted away from the metal atom, defined as the angle between the M–O and O–C(2) vectors. The previously reported range for η-C_3H_5 species is 97–132° [50], and all the τ values recorded here fall within this range. It should be noted, however, that although τ is always obtuse, C(2) is almost always [50,51] found to be closer to the metal atom than is either carbon terminus.

An alternative to τ has been suggested by Muetterties et al. [51], who define δ_1 as the angle between the allylic C_3 plane and the coordination plane of the complex in which the allyl lies. These authors also use the non-allyl coordination plane as a reference for perpendicular Å deviations h_i of the allyl carbon atoms C(i). However, this plane can only be accurately defined for complexes of either square planar or octahedral geometry, i.e. **4** and **10** in the present case. δ_1 for **4**, 120.5°, falls well within the range reported for d^8 square planar complexes. δ_1 for **10**, 105.3°, slightly extends the lower limit of values previously known for d^6 octahedral complexes (105.5–134.1°) and may reflect the relatively small axial ligands, H and Cl, in **10**.

The inequivalence of the h_1 and h_3 parameters in **4** and **10**, with h_1 the closer to h_2, can be described as a rotation of the allyl ligand about the M–O vector such that C(2)–C(3) is brought towards a position in which it would be perpendicular to the aforementioned coordination plane. In the limit of perpendicularity a simplified bonding picture of, for example, **4** would involve $\sigma + \pi$ bonding of the allyl,

TABLE 10

PARAMETERS FOR COORDINATED η^3-1-Ph-C_3H_4

	4	**5**	**10**	**8**
M–C(1)	2.173(3)	2.1739(23)	2.276(6)	2.429(4)
M–C(2)	2.125(4)	2.079(3)	2.178(6)	2.243(4)
M–C(3)	2.124(5)	2.116(3)	2.196(7)	2.311(5)
β (°)	88.88	88.39	88.11	86.72
C(1)–C(2)	1.425(5)	1.412(4)	1.427(8)	1.393(6)
C(2)–C(3)	1.394(6)	1.413(4)	1.378(12)	1.398(6)
C(1)–CR(1)	1.467(5)	1.475(3)	1.483(8)	1.475(6)
C(1)–C(2)–C(3)	119.9(4)	116.49(23)	120.8(8)	116.2(4)
θ (°)	27.3	33.1	52.6	8.5
HR(6)–H(21)	2.25(3)	2.25(4)	2.53(9)	2.17(7)
C(2)–C(1)–CR(1)	123.0(3)	122.97(21)	120.6(6)	125.6(4)
τ (°)	117.6	110.86	113.2	101.9
M–O	1.866	1.851	1.954	2.090
ΔH(12) (°)	−23.8	−29.3	−26.0	−22.6
ΔH(21) (°)	13.4	14.0	10.8	12.6
ΔH(31) (°)	19.7	13.3	1.3	2.1
ΔH(32) (°)	−31.3	−31.1	−32.9	−23.0
δ_1 (°)	120.5	—	105.3	—
h_1	−0.2523	—	0.3495	
h_2	0.3144	—	0.6899	
h_3	−0.3342	—	−0.2480	—

involving C(1) and C(2)=C(3) respectively, to give an overall stereochemistry reminiscent of very many square planar [ML_3(ene)] complexes [52]. In this context it is of interest to note that C(2)–C(3) is significantly shorter than C(1)–C(2) in **4** and **10** whereas in **5** and **8** they are equal in length, and that the C(1)–C(2)–C(3) angles in the former complexes are close to 120°.

The allyl C_3 unit and its phenyl substituent are not coplanar in any of the complexes here analysed. Coplanarity would result in an unacceptably short intraligand HR(6) · · · H(21) contact of ca. 1.8 Å, but this is avoided by a torsion about the C(1)–CR(1) bond. The absolute magnitude of this torsion is θ°. In **8** θ is restricted by intramolecular crowding to 8.5°, but relief from HR(6) · · · H(21) contact comes from an opening up of the C(2)–C(1)–CR(1) angle, 125.6(4)°. In **4** and **5** moderate values of θ, 27 and 33°, are accompanied by moderately wide angles, and it is only when θ is large, as in **10**, that C(2)–C(1)–CR(1) is not significantly deformed from 120°. A further consequence of increasing θ is an increasing loss on conjugation between allyl and phenyl π systems; reflected in the length of the C(1)–CR(1) bond this shows good correlation with θ for the relatively unhindered complexes **4**, **5** and **10**.

Finally, an important aspect of the bonding of an allyl ligand to a metal centre is the effect that rehybridisation of the allyl orbitals has upon the angles of inclination, Δ H, of the terminal H atoms relative to the allyl plane. Although the positions of H atoms determined by X-ray diffraction are notoriously inaccurate [53], considerably more reliability attends angles involving C–H vectors [54]. Thus, the *anti* hydrogens H(12) and H(32) are consistantly bent away from the metal (Δ H < 0) by between −22 and −33°, whilst H(21) bends towards M by between 11 and 14°. Similar

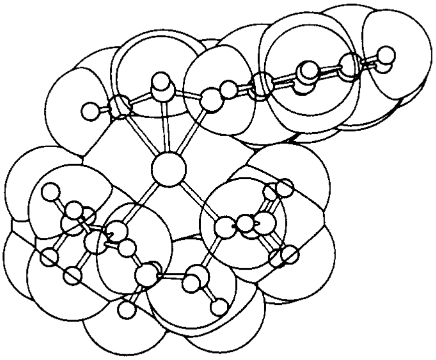


Fig. 4. Space filling diagram of the cation of **4**.

values have previously been recorded in other accurately studied allyl complexes [55–61]. Greater variation, however, is found in the inclination angles of H(31). Although consistently leaning towards the metal atom this *syn* H does so by between 1 and 20°.

Intra- and intermolecular contacts. The structural studies of **4**, **5** and **8** all show that the substituted carbon atom, C(1), is further from the metal than is the unsubstituted C(3). Clearly, this asymmetry could be said to result simply from increased intramolecular interligand crowding in that part of the molecule caused by substitution of the relatively bulky C_6H_5 group for H.

In the cation of **4** there exist two contacts, H(93) · · · CR(1) 2.746(6) and H(93) · · · CR(6) 2.937(7) Å (c.f. sum of Van der Waals radii for H and aromatic carbon of 3.05 Å), that could certainly contribute to the asymmetry observed in metal–allyl bonding. A space filling representation of the cation (Fig. 4) shows touching spheres in this region.

However, an equivalent diagram of **5** (Fig. 5) strikingly demonstrates that the (η-C_5H_5) and (η-1-Ph-C_3H_4) ligands are well separated; consequently no intramolecular steric factor can be invoked to explain the observed hinging of the latter. The second paper in this series [7] offers a rationalisation based upon the results of EHMO calculations.

In **8** intramolecular interligand interaction is dominated by quasi-graphitic con-

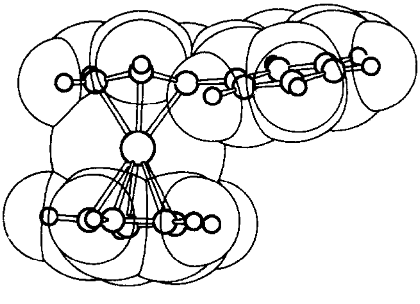


Fig. 5. The space filling diagram of **5**. For clarity only the major component of the (η-C_5H_5) ligand is shown.

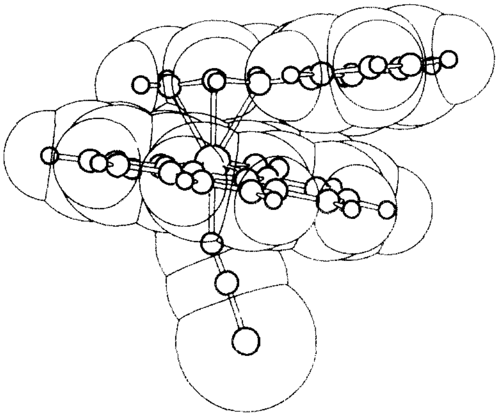


Fig. 6. A space filling diagram of **8**.

tact between the phenyl ring and part of the phenanthroline ligand, and is clearly seen in Fig. 6. The two aromatic systems are nearly parallel (dihedral angle 17.4°) and centroids of the two six-membered rings, CR(1)–CR(6) and N(2)C(15)-C(11)C(12)C(13)C(14) are only 4.062(5) Å apart, ca. 4.7 Å having been calculated [62] as representing the onset of interaction. It is this contact that presumably restricts θ to 8.5° in **8**.

Crystal packing diagrams for **4**, **5** and **8** have been deposited (Figs. 7–9, respectively), as have full details of intermolecular contacts. In the crystal **4** exists are reasonably well separated ion pairs. There is no graphitic packing between phenyl rings of symmetry-related cations, and only minimal H · · · H and H · · · CR contacts. In **5** molecules are even more isolated. The crystal structure of **8**, however, features strong graphitic packing between the bicyclic sequence N(1)C(5)-C(6)C(7)C(8)C(4)C(15)C(11)C(10)C(9) and its (necessarily parallel) image through the inversion centre at 0 1/2 1/2.

Supplementary material available

Least-squares planes data, non-bonded contacts, thermal parameters, crystal packing diagrams, and listings of structure factor amplitudes are available from the authors.

Acknowledgements

We thank the Chemistry Department of the University of Edinburgh for a studentship (N.W.M.), and Johnson Matthey plc for a loan of palladium chloride.

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