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FORMATION AND STRUCTURE OF BIS(DIPHENYL-PHOSPHINO)ETHANE BIS(INDENYL)MOLYBDENUM(II), A COMPOUND WITH ONE η^3 AND ONE η^5 INDENYL LIGAND (*)(**)(***)

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Summary - The interaction between MoI_3(dppe)(THF) [dppe = bis(diphenylphosphino)ethane] and excess C_9H_7Na (indenylsodiurn) produces $(\eta\text{-}C_9H_7)_2Mo(dppe)$, which has been characterized by X-ray diffraction as toluene solvate. Crystal data for $(\eta\text{-}C_9H_7)_2Mo(dppe)\cdot 1/2C_7H_5$: monoclinic, space group $I2/a$, a = 20.333(3), b =15.507(2), c = 24.543(3) Å, β = 105.09(1)°, V = 7472(2) Å^3, Z = 8, d_c = 1.370 g cm^{-3}, μ (Mo-$K\alpha$) = 4.67 cm^{-1}, R = 0.0293, R_w = 0.0394 for 641 parameters and 3757 data with $F_o^2 \geq 3\sigma(F_o^2)$. The structure shows that each indenyl ring is bonded to the Mo atom through the five-membered ring, but although one ring adopts the η^5 bonding mode, the other is "slipped to achieve a conformation with only three carbon atoms directly attached to the metal (η^3 bonding mode). The two rings rapidly exchange in solution on the NMR time scale and the exchange cannot be frozen out by cooling to -90 °C.

(*) Work supported by the Donors of the Petroleum Research Fund. administered by the American Chemical Society.

(**) Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained upon request from: The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

(***) Dedicated to Professor Lamberto Malatesta on the occasion of his 80th birthday.

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The ability of the indenyl group to bind in different fashions to transition metals has always attracted considerable attention, mostly in relation to the involvement of "ring slipped" intermediates in organometallic reactions.[1] Typically, the arrangement of the indenyl ring is dictated by the electronic requirements of the transition metal (18-electron rule). The two most typical modes of binding are the η^5 mode (5-electron donor in the covalent model) and the η^3 mode (3-electron donor). There are a number of interesting cases where the metal is contemporarily coordinated to two indenyl rings. If it turns out that a total of 8 electrons are necessary to reach a closed shell configuration, either one of two things can occur: either one indenyl ring binds in an η^5 mode and the other binds in an η^3 mode, or they both partially "slip" from the ideal η^5 mode. The first situation is found for $(\eta\text{-}C_9H_7)_2W(CO)_2$,[2] whereas the second one has been observed for $(\eta\text{-}C_9H_7)_2Ni$.[3] In this contribution, we report the formation and structural characterization of a new compound of this type, $(\eta\text{-}C_9H_7)_2Mo(dppe)$, which adopts a static structure analogous to that of the dicarbonyltungsten compound.

EXPERIMENTAL

All operations were carried out under an atmosphere of dinitrogen with standard glove box and Schlenk line techniques. Solvents were purified by standard methods and distilled under dinitrogen prior to use. NMR measurements were carried out on Bruker WP200, AF20P, and AM400 spectrometers and the resonances were referenced downfield of the residual protio portion of the deuterated solvent; EPR, Bruker ER200. Elemental analyses were by Midwest Microlab, Phoenix, Arizona. The compound $MoI_3(THF)_3$ was prepared by the literature procedure.[4] A stock solution of indenylsodium in THF was prepared by refluxing metallic sodium with indene and its concentration was established by acid-base titration. Dppe was purchased from Strem and used as received.

FORMATION OF $(\eta\text{-}C_9H_7)_2Mo(dppe)$

$MoI_3(THF)_3$ (0.497 g, 0.717 mmol) and dppe (0.286 g, 0.717 mmol) were placed in 30 ml of THF. The mixture was stirred overnight to allow the formation of a red solution of $MoI_3(dppe)(THF)$ as described earlier.[5] To this solution was added indenylsodium (3.15 ml, 0.683 M in THF, 2.15 mmol). The resulting solution was allowed to reflux for 30 min, resulting in a colour change from red to yellow-brown. After cooling, the solvent was completely removed by evaporation and the residue was treated with toluene (20 ml). The resulting solution was filtered and concentrated by evaporation to ca. 5 ml. Addition of 20 ml of heptane to this solution caused the precipitation of the product in microcrystalline form. This was filtered off, washed with heptane, and dried *in vacuo*. Yield 219 mg

(42%). *Elem. anal.*, found % (calcd for $C_{44}H_{33}MoP_2$): C, 72.4 (72.9); H, 5.6 (5.2). ^{1}H-NMR (r. t., C_6D_6), δ: 7.2-6.9 (tn, 20 H, Ph), 6.68 (m, 8 H, indenyl H5-H8), 5.84 (tt, J_{HH} = 3.0 Hz, J_{HP} = 4.8 Hz, 2 H, indenyl-H2), 3.53 (br, 4 H, indenyl H1/3), 1.99 ppm (d, J_{PH} = 12.6 Hz, 4 H, PCH_2CH_2P). ^{31}P NMR (r. t., C_6D_6), δ: 63.0 ppm (s). ^{13}C NMR (r. t., CD_2Cl_2), δ (refer to I for indenyl carbon assignments): 139.9 (d, J_{PC} = 31.4 Hz, *i*-Ph), 133.0 (t, $J_{PC} \leq 3$ Hz, C4/9), 132.3 (virtual triplet, J_{PC} = 8 Hz, *o*-Ph), 129.3 (s, *p*-Ph), 128.2 (virtual t, J_{PC} = 6 Hz, *m*-Ph), 122.0, 121.2 (both s, C5-9), 92.3 (s, C2), 72.0 (s, Cl/3), 27.6 ppm (dd, $J_{PC}+J_{P'C}$ = 40.2 Hz, $J_{PC}-J_{P'C}$ = 3 Hz, CH_2).

The compound is quite soluble in aromatic hydrocarbons and CH_2Cl_2, sparingly soluble in heptane and acetone, and decomposes in $CHCl_3$. A single crystal for the X-ray analysis was obtained by slow diffusion of heptane into a toluene solution. By this procedure, one molecule of toluene per two molecules of complex is included in the crystal lattice. The presence of interstitial solvent was also indicated by the weak ^{1}H NMR resonance at δ 2.12 ppm for CH_3 and by the ^{13}C NMR resonance at δ 23.1 ppm for CH_3.

X-RAY CRYSTALLOGRAPHY

The sample crystal was mounted on a glass fibre and covered with a thin layer of epoxy resin. Geometric and intensity data were taken via routine methods. Following autoindexing, the body-centred setting of the doubly primitive cell was chosen, in order to have a reduced oblique net for the ac-plane. For verification of the lattice parameters and the Laue group, normal-beam oscillation photos were taken for seven axes - the three cell edges, the three face-diagonals of the cell, and one body diagonal, [111].

During intensity data collection, three monitor reflections were measured every 180 minutes. These showed almost negligible variations in their intensities as the data collection progressed. Measurements for an empirical absorption correction comprised nine complete ψ-scans as well as 25 sets each comprising the measurement of one reflection of moderate intensity and all of its symmetry equivalents. During the application of the absorption correction,[6] a value of 0.3 was used for the spherical parameter of μR.

Information related to the structure determination is summarized in table 1. The structure was solved by direct methods and refined by alternate least-squares refinements and difference Fourier maps. All hydrogen atoms of the complex $(\eta\text{-}C_7H_9)_2Mo(dppe)$ were located in difference maps and were refined independently - each with its own isotropic displacement parameter. A set of atomic sites located on and around a crystallographic twofold axis was modelled as a group of four disordered toluene molecules, each partially occupying this interstitial site. In the refinement of the toluene moieties, loose observational restraints were used for the C-C bond distances and for the *meta*-C⋯C

distances. The full-matrix refinement converged with the residuals given in table 1. Atomic coordinated are listed in table 2, whereas selected bond distances and angles are collected in table 3.[a]

TABLE 1 - CRYSTAL DATA FOR $(\eta\text{-}C_9H_7)_2Mo(Dppe)\text{-}l/2C_7H_8$

Formula	$MoP_2C_{44}H_{38}\cdot 0.5\ C_7H_8$
*f*w	770.74
Space group	$I2/a^a$
Systematic absences	(hkl): $h+k+l \neq 2n$; $(h0l)$: $h\ (l) \neq 2n$
a, Å	20.333(3)
c, Å	15.507(2)
c, Å	24.543(3)
β, deg	105.09(1)
V, Å^3	7772(2)
Z	8
d_{calc}, g/cm^3	1.370
Crystal size, mm	0.55 x 0.43 x 0.32
μ(Mo *K*α), cm^{-1}	4.67
Transmission factors: max, min.	0.592, 0.544
Data collection instrument	Stoe/Siemens AED-2
Radiation (graphite monochromated)	Mo *K*α (λ = 0.71073 Å)
Orientation reflecns: no.; range (2θ), deg	25; 24.6-34.9
T, °C	19±1
Scan method	ω-2θ
No. of unique data	4882
No. of data with $F_o^2 \geq 3\sigma(F_o^2)$	3735
No. of parameters refined	641
R^b	0.0293
$R_w{}^c$	0.0394
Quality of fit indicator^d	1.022
Largest shift/esd, final cycle	0.35
Lasest peak/hole, e/Å^3	0.33, -0.29

([a]) Non-standard setting of space group *C*2/*c* (No. 15). The coordinates of general equivalent positions are (0,0,0; ½,1/2,1/2); (*x*,*y*,*z*; 1/2+*x*,-*y*,*z*); and positions generated by the application of (-*x*,-*y*,-*z*). ([b]) $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. ([c]) $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ([d]) Quality of fit = $[\Sigma w(|F_o|-|F_c|)^2/(N_{observns}-N_{parameters})]^{1/2}$.

TABLE 2 - ATOMIC POSITIONA1. PARAMETERS (x10^4) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å^{2}x10^3) FOR $(\eta\text{-}C_9H_7)_2Mo(dppe)\cdot 1/2\ C_7H_8$

Atom	*X/a*	*Y/b*	*Z/c*	$U_{eq}{}^a$
Mo(1)	5224(1)	3664(1)	2728(1)	34(1)

[a] Supplementary material (full tables of bond distances and angles, anisotropic displacement parameters, and a list of observed and calculated structure factors have been deposited with the Editor and can be obtained from Società Chimica Italiana, Viale Liegi 48, I-00198 Roma, Italy, by full citation of the present article.

P(1)	5743(1)	3421(1)	1942(1)	36(1)
P(2)	6173(1)	2698(1)	3147(1)	38(1)
C(1)	5223(2)	2934(2)	1276(1)	38(1)
C(2)	5141(2)	2053(3)	1214(1)	50(2)
C(3)	4723(2)	1705(3)	727(2)	61(2)
C(4)	4397(2)	2231(4)	301(2)	68(2)
C(5)	4465(2)	3106(3)	355(2)	61(2)
C(6)	4878(2)	3456(3)	838(2)	48(2)
C(7)	6121(2)	4294(2)	1615(1)	40(1)
C(8)	5846(2)	5110(3)	1544(2)	57(2)
C(9)	6069(3)	5737(3)	1242(2)	66(2)
C(10)	6584(2)	5575(3)	1002(2)	65(2)
C(11)	6875(2)	4774(4)	1062(2)	69(2)
C(12)	6649(2)	4135(3)	1365(2)	58(2)
C(13)	6472(2)	2651(3)	2127(2)	43(1)
C(14)	6418(2)	2053(3)	2600(2)	43(1)
C(15)	6096(2)	1876(2)	3667(2)	42(1)
C(16)	6258(2)	1014(3)	3629(2)	50(2)
C(17)	6201(3)	433(3)	4044(2)	66(2)
C(18)	5981(3)	706(3)	4500(2)	69(2)
C(19)	5812(3)	1561(3)	4545(2)	69(2)
C(20)	5270(2)	2140(3)	4127(2)	60(2)
C(21)	7009(2)	3184(2)	3496(2)	40(1)
C(22)	5432(2)	2871(3)	3998(2)	51(2)
C(23)	8043(2)	3245(3)	4238(2)	62(2)
C(24)	8271(2)	3935(3)	3987(2)	60(2)
C(25)	7872(2)	4248(3)	3491(2)	53(2)
C(26)	7242(2)	3881(2)	3250(2)	45(1)
C(27)	4543(2)	2576(3)	2954(2)	53(2)
C(28)	4661(2)	2477(3)	2412(2)	46(2)
C(29)	4256(2)	3139(3)	2077(2)	47(2)
C(30)	3695(2)	3331(3)	2333(2)	49(1)
C(31)	3084(2)	3752(3)	2137(2)	63(2)
C(32)	2634(3)	3929(3)	2474(3)	73(2)
C(33)	2804(3)	3485(3)	3000(3)	75(2)
C(34)	3430(3)	3061(3)	3219(2)	63(2)
C(35)	3871(2)	2984(3)	2880(2)	50(2)
C(36)	4565(2)	4795(3)	2906(2)	47(2)
C(37)	4999(2)	5098(2)	2583(2)	44(1)
C(38)	5683(2)	5042(2)	2911(2)	42(1)
C(39)	5663(2)	4747(2)	3464(2)	44(1)
C(40)	6182(3)	4656(3)	3973(2)	55(2)
C(41)	5995(3)	4442(3)	4453(2)	72(2)
C(42)	5318(3)	4275(3)	4437(2)	74(3)
C(43)	4807(3)	4323(3)	3958(2)	63(2)
C(44)	4966(2)	4592(2)	3454(2)	44(1)
C(45) [b]	2500	2810(11)	0	131(15)
C(46) [b]	2723(5)	2293(8)	483(3)	192(9)
C(47) [b]	2619(12)	1418(9)	476(5)	179(16)

C(48) [b]	2500	921(11)	0	185(20)
C(49) [b]	2500	3670(11)	0	156(17)
C(50) [b]	2500	1775(11)	0	147(18)
C(51) [b]	2773(8)	3171(9)	455(5)	166(15)
C(52) [b]	3037(25)	2713(13)	991(6)	225(39)
C(53) [b]	3074(19)	1859(12)	982(6)	248(40)

([a]) The equivalent isotropic displacement parameter, U_{eq}, is calculated as: $U_{eq} = 1/3\ \Sigma U_{ij} a_i a_j a_i^* a_j^*$. ([b]) Disordered interstitial toluene molecules. The model used was refined with the following site occupancies: 0.25 for C(45), C(43), C(49), C(50), C(52), and C(53); 1.00 For C(46); and 0.50 for C(47) and C(51).

TABLE 3 - SELECTED DISTANCES (Å) AND ANGLES (degrees) AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $(\eta\text{-}C_9H_7)_2Mo(dppe)\cdot l/2C_7H_8$

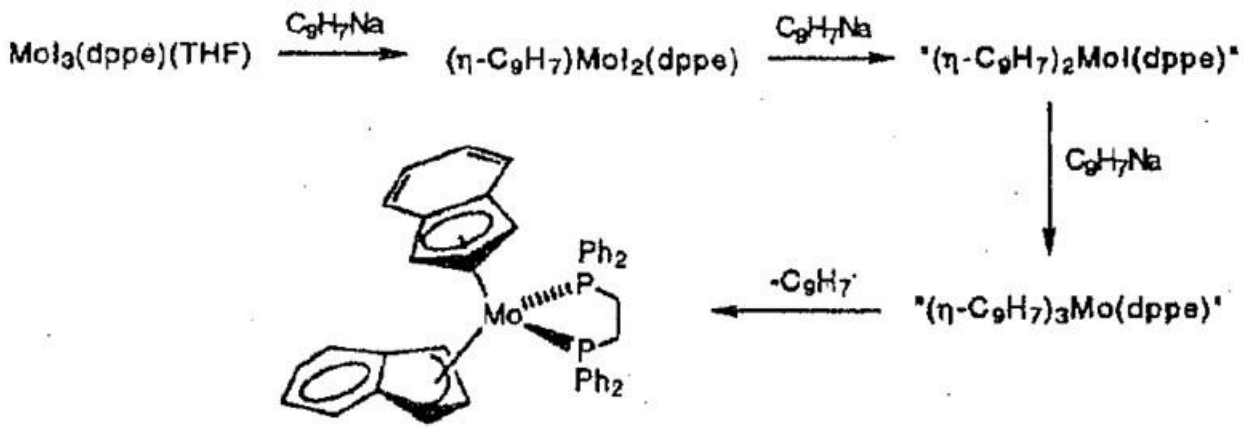
a) Distances			
Mo(1)-P(1)	2.457(1)	P(1)-C(13)	1.865(4)
Mo(1)-P(2)	2.448(1)	P(2)-C(14)	1.842(4)
Mo(1)-C(27)	2.340(5)	P(2)-C(15)	1.839(4)
Mo(1)-C(28)	2.200(4)	P(2)-C(21)	1.852(3)
Mo(1)-C(29)	2.336(3)	C(27)-C(28)	1.421(7)
Mo(1)···C(30)	3.050(4)	C(27)-C(35)	1.474(6)
Mo(1)···C(35)	3.060(4)	C(28)-C(29)	1.434(5)
Mo(1)-C(36)	2.315(4)	C(28)-C(30)	1.468(6)
Mo(1)-C(37)	2.279(4)	C(30)-C(35)	1.404(6)
Mo(1)-C(38)	2.327(4)	C(36)-C(38)	1.411(7)
Mo(1)-C(39)	2.458(3)	C(36)-C(44)	1.415(5)
Mo(1)-C(44)	2.451(4)	C(37)-C(38)	1.417(5)
P(1)-C(1)	1.860(3)	C(38)-C(39)	1.442(6)
P(1)-C(7)	1.841(4)	C(39)-C(44)	1.431(6)
b) Angles			
P(1)-Mo(1)-P(2)	77.5(1)	C(27)-C(28)-C(29)	104.2(4)
P(1)-Mo(1)-C(28)	83.4(1)	C(28)-C(29)-C(30)	107.2(4)
P(2)-Mo(1)-C(28)	85.2(1)	C(29)-C(30)-C(31)	132.7(4)
P(1)-Mo(1)-C(37)	97.9(1)	C(29)-C(30)-C(35)	107.4(3)
P(2)-Mo(1)-C(37)	140.1(1)	C(31)-C(30)-C(35)	119.8(4)
C(26)-Mo(1)-C(37)	134.1(1)	C(27)-C(35)-C(30)	106.1(4)
Mo(1)-P(1)-C(1)	119.1(1)	C(27)-C(35)-C(34)	133.8(4)
Mo(1)-P(1)-C(7)	122.9(1)	C(30)-C(35)-C(34)	120.1(4)
C(1)-P(1)-C(7)	97.0(2)	C(37)-C(36)-C(44)	108.6(4)
Mo(1)-P(1)-C(13)	112.6(1)	Mo(1)-C(37)-C(36)	73.5(2)
C(1)-P(1)-C(13)	100.9(2)	Mo(1)-C(37)-C(38)	73.9(2)
C(7)-P(1)-C(13)	100.4(2)	C(36)-C(37)-C(38)	108.9(3)
Mo(1)-P(2)-C(14)	111.0(1)	C(37)-C(38)-C(39)	106.9(4)
Mo(1)-P(2)-C(15)	121.0(1)	C(38)-C(39)-C(40)	131.6(4)
C(14)-P(2)-C(15)	102.6(2)	C(38)-C(39)-C(44)	107.9(3)
Mo(1)-P(2)-C(21)	118.2(1)	C(40)-C(39)-C(44)	120.3(4)
C(14)-P(2)-C(21)	99.7(2)	C(36)-C(44)-C(39)	107.6(4)
C(15)-P(2)-C(21)	101.2(2)	C(36)-C(44)-C(43)	133.4(4)
C(28)-C(27)-C(35)	108.1(4)	C(39)-C(44)-C(43)	119.0(4)
Mo(1)-C(28)-C(27)	77.2(2)		
Mo(1)-C(28)-C(29)	76.8(2)		

RESULTS AND DISCUSSION

SYNTHESIS

The title compound was initially obtained as a by-product of the reaction between $MoI_3(dppe)(THF)$[5] and one equivalent of C_9H_7Na, which was carried out with the intent to produce $(\eta\text{-}C_9H_7)MoI_2(dppe)$. This is indeed the main product of the reaction, and its properties will be reported in a future contribution within the framework of our current studies of the halide ligand substitution mechanism in paramagnetic Mo(III) organometallic complexes.[7,8] From the toluene washings, the title compound was obtained in small yields. When the reaction was repeated with three, rather than one, equivalents of indenyl sodium, then $(\eta\text{-}C_9H_7)_2Mo(dppe)$ was the major product of the reaction and was isolated as a pure material. This suggests that the reaction proceeds either as shown in the scheme or, alternatively, the replacement of the last iodide ligand and the elimination of the indenyl radical could be reversed in order; that is, an indenyl radical may be expelled first from the "$(\eta^5\text{-}C_9H_7)_2MoI(dppe)$" intermediate to produce a l6~electron "$(\eta^5\text{-}C_9H_7)MoI(dppe)$" intermediate, followed by exchange of the last iodide ligand.

SCHEME



These mechanistic schemes and the overall process which results in metal reduction to the +2 formal oxidation state are related to our recently reported rnethylation of $CpMoCl_2(PMe_{32}$ to afford $CpMo(CH_3)(PMe_3)_3$ with elimination o fa methyl radical.[9,10] This observation reinforces our conclusion that 17-electron Mo(III) compounds of the $(\eta^5\text{-ring})MoX_2L_2$ type are energetically stabilized by π donation from halide ligands and will not be stable when the halides are completely replaced by carbyl ligands.[9] Of relevance to the chemistry described here is also the report by Jolly

at al.[11] that the reaction between the Mo(IV) $(\eta\text{-}C_3H_5)_3MoCl$ compound and CpNa involves elimination of an allyl radical with formation of the Mo(III) product $CpMo(\eta\text{-}C_3H_5)_2$.

X-RAY STRUCTURE

A single crystal X-ray analysis has established the molecular structure of the compound. A general view of the molecule is shown in figure 1. The most important feature of the structure is the coordination mode of the two indenyl rings, which are emphasized in the views illustrated in figures 2 and 3. One indenyl ring is significantly slip-folded with three atoms of the five-membered ring significantly closer to the metal than the other two, whereas the other seems to have the five-membered ring symmetrically placed over the metal atom. Thus, to a first approximation, the coordination modes of the two indenyl groups could be classified as "η^3" and "η^5", respectively, to give an 18-electron count for the molecule. The coordination mode can be more quantitatively analyzed in terms of several structural parameters, i.e. the slip parameter, $\Delta_{M\text{-}C}$ (the difference in the average bond lengths of the metal to the ring junction carbons, *i.e.* C4 and C9, and the metal to the adjacent carbon atoms of the five-membered ring, *i.e.* C1 and C3; refer to structure **I**), the hinge angle, HA (angle between the planes C1, C2, C3 and C1, C3, C4, C9), and the fold angle, FA (angle between the plane C1, C2, C3 and the least-squares plane of the six-membered ring, i.e. C4-C9).

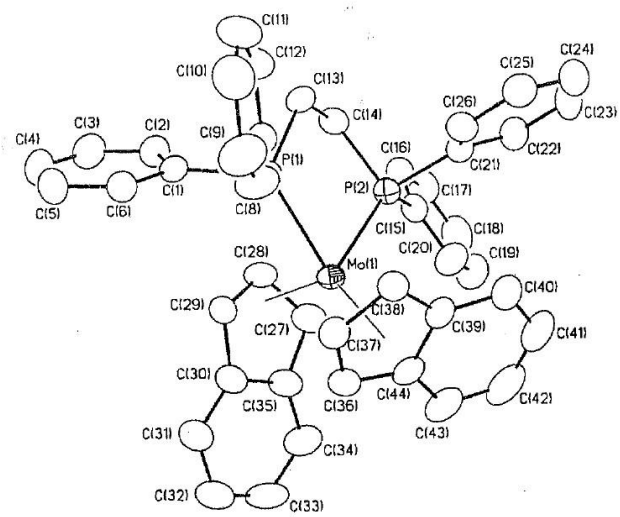


Fig. l. A view of the $(C_9H_7)_2Mo(dppe)$ molecule with the numbering scheme employed. Atoms C(7), bonded to P(1), C(8), and C(12), have not been labelled because of space constraints.

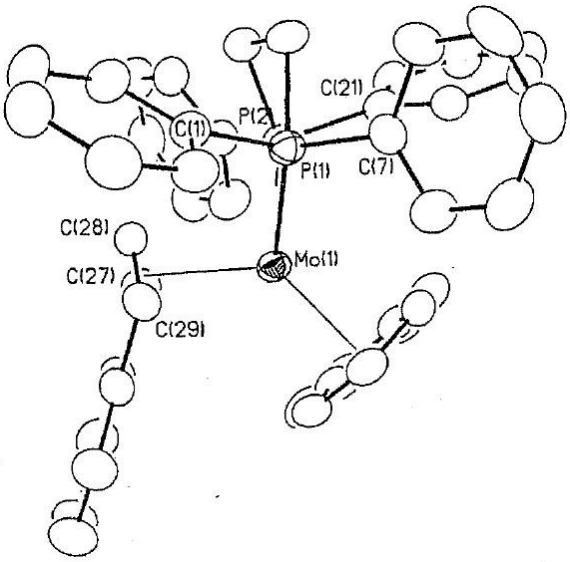


Fig. 2. Projection of the $(C_9H_7)_2Mo(dppe)$ molecule emphasizing the η^3 coordination mode of one of the two indenyl rings, through the C(27), C(38), and C(29) atoms.

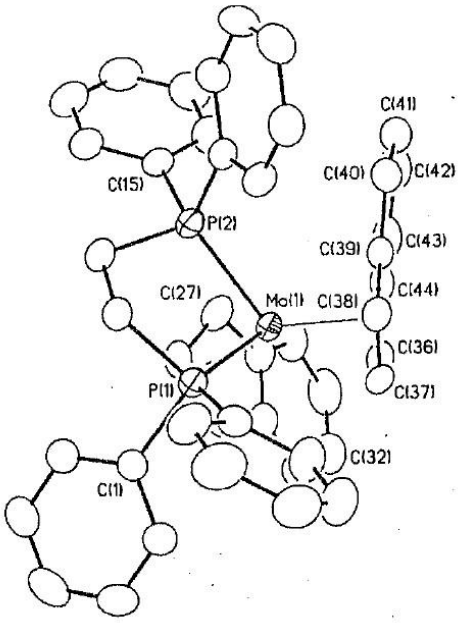
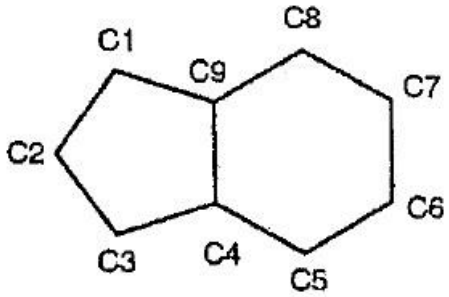


Fig. 3 - Projection of the $(C_9H_7)_2Mo(dppe)$ molecule emphasizing the η^5 coordination mode of one of the two indenyl rings, through the C(36), C(37), C(38), C(39) and C(44) atoms.



I

The slip distortion parameters for our compound are 0.717(4) Å for the more distorted ligand (C27-C35) and 0.134(4) Å for the other ligand (C36-C44). The higher value compares with those reported for other η^3-coordinated indenyl rings, *i.e.* 0.79(1) Å for[12] $(\eta\text{-}C_9H_7)Ir(PMe_2Ph)_3$, 0.698(7) Å for[13] $[(\eta\text{-}C_9H_7)Fe(CO)_3]^-$, and 0.72(2) Å for[2] the slipped ring in $(\eta\text{-}C_9H_7)_2W(CO)_2$. The smaller value appears significantly larger than those found for other compounds where the indenyl has been described as having an η^5-coordination mode, *e.g.* 0.030(4) Å for[3] $(\eta\text{-}C_9Me_7)_2Fe$, and 007(2) Å for the less distorted group in[2] $(\eta\text{-}C_9H_7)_2W(CO)_2$. We can tentatively attribute this greater distortion of the η^5 indenyl ring to unfavourable steric interactions in the crowded coordination sphere. The angular parameters HA and FA are also consistent with at major distortion in the first indenyl ligand and a very small distortion in the second one. HA angles are 25.5 and 3.7°, whereas FA angles are 26.5 and 8.4° for η^3 and η^5 rings, respectively. FA angles for the above-mentioned molecules containing η^3-indenyl groups are in the 22-26° range. Again, HA and FA angles for the η^5 ring are not as low as the values found for other η^5 indenyl structures, indicating that steric interactions are likely responsible for this distortion. As it is evident from figures 1 and 3, the benzene ring defined by atoms C39-C44 is at close contact with the phenyl groups on atom P2. The closest contact between these groups [C(40)···C(21), 3.229(6) Å; C(40)···C(26), 3.351(7) Å] are near the lower limit for the sum of van der Waals' radii for aromatic groups, indicating that a closer approach of the two groups would be quite unfavourable energetically. The pattern of C-C distances in the two indenyl five-membered rings also reflects the observed distortions. The slip-folded ring has elongated C-C bonds between reach ring junction carbon atom and the neighbouring hinge carbon atom [C(27)-C(35), 1.474(6) Å; C(29)-C(30), 1.468(6) Å], and a shortened ring junction C-C bond [C(30)-C(35), 1.404(6) Å] with respect to the C-C bonds in the slipped ring η^3-allyl moiety and in the other, η^5-coordinatcd, five-membered ring, all of which are in the 1.411-1.442 Å range.

The Mo-P distances [average 2.452(5) Å] compare with those found for other dppe complexes of Mo(II), *e.g.* 2.496(4) and 2.439(5) Å in[14] *cis*-CpMoCl(CO)(dppe), 2.50 Å (average) in[15] $[CpMo(dppe)(\eta\text{-}C_6H_8)]^+$, and for complexes of similar diphosphines, *e.g.* 2.402(1) and 2.437(2) Å in[16] *trans*-$CpMoCl(CO)[(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2]$, and 2.423(7) and 2.461(2) Å in[17] *cis*-$[CpMo(CO)(\eta\text{-}C_2H_4)[(MeO)_2PCH_2CH_2P(OMe)_2]]^+$.

Another way to look at the structure of the title compound is as a four-legged piano stool where the η^5-indenyl ring represents the stool and the η^3 ring binds to two cis legs. In this respect, the molecule is analogous to many cyclopentadienyl-allyl complexes of Mo(II) reported in the literature, for instance $(\eta^5\text{-}C_9H_7)Mo(\eta^3\text{-}C_3H_5)(CO)_2$,[18] $(\eta^5\text{-}C_9H_7)Mo(\eta^3\text{-}1\text{-}C_3H_4Me)[P(OMe)_3]_2$,[19] $CpMo(\eta^3\text{-}1\text{-}C_3H_4Me)[P(OMe)_3]_2$,[19] $CpMo(\eta^3\text{-}1\text{-}C_3H_4Me)(dppe)_2$,[20] and Cp- and $Cp^*Mo(\eta^3\text{-}C_3H_5)(PMe_3)_2$,[10] although none of these, to the best of our knowledge, have been characterized structurally. Viewed

as a four-legged piano stool compound, the title compound shows a supine orientation of the allyl functionality of the η^3 indenyl group, which is what has been suggested for compounds Cp- and Cp*Mo(η^3-C_3H_5)(PMe_3)$_2$ on the basis of ^{1}H-NOE difference NMR experiments.[10]

NMR CHARACTERIZATION

Both ^{1}H- and ^{13}C NMR spectra clearly indicate that the two indenyl rings are in fast exchange with respect to the time scale of the techniques, even at the lowest temperatures we could reach in the toluene-d_8 solvent. A single resonance is observed for each set of corresponding nuclei (H_2, $H_{1/3}$, H_{4-8}, C_2, $C_{4/9}$, $C_{5/8}$, and $C_{6/7}$) of the two rings. In addition, a doublet is observed for the phosphine methylene protons whereas an AA'BB'XX' system would be expected for the rigid structure. A rapid fluxional behaviour was also reported for the similar (η-C_9H_7)$_2$W(CO)$_2$ complex on the basis of the room temperature ^{1}H NMR, but the compound could not be investigated at lower temperatures or by ^{13}C NMR due to scarce solubility.[2] The position of the proton resonances for this compound (δ 6.6, 4.78, and 3.4 ppm for the benzene ring protons, H_2, and $H_{1/3}$, respectively)[2] compare quite closely with those at δ 6.68, 5.84, and 5.53 ppm observed for the corresponding protons of the title compound.

The chemical shift of the indenyl ^{13}C NMR resonances has been related to the hapticity of the ring, the resonance of the ring junction carbon atoms (C4 and C9 in **I**) being most sensitive to the amount of slip-fold distortion.[21] We find this resonance at δ 133.0 ppm, which is at an intermediate position between the shifts for η^3 indenyl complexes [*e.g.* δ 156.7 ppm for (η-C_9H_7)Ir(PMe_3)$_3$ and 157.3 for [(η-C_9H_7)Fe(CO)$_3$]$^-$ [12,13] and for η^5 indenyl complexes [*e.g.* δ 111.01 ppm for (η-C_9H_7)lr(η-cyclooctene)$_2$ and 121.15 for (η-C_9H_7)lr(PEt_3)$_2$],[12] and it corresponds quite closely with the position found for the isoelectronic bis(indenyl)nickel complex (δ 134.3 ppm).[3]

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