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Preparation of cis -[MoI₄(Ph₂PCH₂CH₂PPh₂)]⁻ and structure of (THF)₃Na(μ-I)₃MoI(Ph₂PCH₂CH₂PPh₂) with a new coordination environment around sodium ☆

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Abstract

The complex cis -[MoI₄(dppe)]⁻ is obtained in good yields from $trans$ -[MoI₄(THF)₂]⁻ and dppe (dppe = 1,2-bis(diphenylphosphino)ethane) or directly from the interaction of MoI₃(THF)₃, I⁻ and dppe and has been isolated as the PPh₄ and Na(THF)₃ salts. The sodium salt has been characterized crystallographically: monoclinic $P2_1/n$, $a = 12.790(2)$, $b = 16.512(7)$, $c = 23.117(4)$ Å, $\beta = 103.65(1)^\circ$, $V = 4744(1)$ Å³, $D_{calc} = 1.84$ g cm⁻³, $Z = 4$, $R = 0.039$ for 4485 independent observed reflections ($F_o^2 \geq 3\sigma(F_o^2)$). The structure features an octahedral coordination around both Na and Mo atoms in an overall face-sharing bioctahedral structure with the two metals being bridged by three iodide ligands. This is an unprecedented case of a structure containing an O₃I₃ coordination for Na ions and iodide ligands bridging sodium with a transition metal. The ¹H NMR properties of the complex are also examined in comparison to those of the MoI₃(dppe)(THF) precursor.

Keywords: Crystal structures; Molybdenum complexes; Iodide complexes; Diphosphine complexes; Sodium complexes

1. Introduction

After its synthesis by oxidative decarbonylation [1], MoI₃(THF)₃ has served as a starting material for the preparation of a variety of derivatives, among which are mononuclear octahedral *mer*- and *fac*-MoI₃L₃ (L = PMe₃, PEt₃; L₃ = (dppe)(THF), (dppe)(PMe₃)) [1,2], dinuclear face-sharing bioctahedral [Mo₂I₇(PMe₃)₂]⁻ and Mo₂I₆(PMe₂Ph)₃ [3] and organometallic derivatives CpMoI₂L₂ (Cp = η⁵-C₅H₅; L = PMe₃; L₂ = dppe) [4]. Mononuclear anionic complexes of the type $trans$ -[MoI₄L₂]⁻ (L = PEt₃, PEt₂Ph) also exist [1,5], although these were originally made from different precursors. Recently, the reaction between MoI₃(THF)₃ and I⁻ to afford $trans$ -[MoI₄(THF)₂]⁻, which loses THF in a non-coordinating solvent to afford trinuclear clusters, has been described [6]. Here, we report the formation and structure of an octahedral tetraiodo-molybdenum complex with a *cis* configuration, which has been achieved by utilizing the chelating ligand dppe. Iodide ligands are known to be particularly suitable in coordination chemistry, functioning as bridging ligands.

The structure presented here exhibits an unusual feature in that three iodide ligands bridge a molybdenum atom and a sodium atom.

2. Experimental

All operations were carried out under an atmosphere of dinitrogen using standard Schlenk line techniques. Solvents were dehydrated by conventional methods and distilled directly from the dehydrating agent prior to use. ¹H NMR spectra were obtained with Bruker WP200 and AF200 spectrometers; the peak positions are reported downfield of TMS as calculated from the residual solvent peaks. The elemental analyses were by M-H-W Laboratories, Phoenix, AZ. MoI₃(THF)₃ was prepared according to the literature procedure [1].

2.1. Reaction between MoI₃(dppe)(THF) and PPh₄I. Synthesis of [PPh₄][MoI₄(dppe)]

MoI₃(dppe)(THF) was prepared in situ as described earlier [2] from MoI₃(THF)₃ (570 mg, 0.82 mmol) and dppe (330 mg, 0.83 mmol) in 30 ml of THF. When the reaction was complete, as evidenced by the complete dissolution of the Mo starting complex, the solution was evaporated to dryness. In another Schlenk flask a

☆ Dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

* Corresponding author.

solution of PPh₄I (390 mg, 0.83 mmol) in 25 ml of CH₂Cl₂ was prepared. This solution was then transferred into the flask containing the Mo complex and stirred at room temperature. The solid dissolved completely to afford a dark red solution. The reaction was complete in 30 min, as verified by NMR monitoring. The solution was concentrated to ~10 ml and cooled to -20 °C, to afford the red microcrystalline product, which was then filtered off, washed with pentane and dried under vacuum. Yield 450 mg (40%). Diffusion of a pentane layer into the mother solution gave additional red solid to bring the total yield to 852 mg (75%). *Anal.* Calc. for C_{50.5}H₄₅ClI₄MoP₃ (PPh₄[MoI₄(dppe)]·½CH₂Cl₂): C, 43.83; H, 3.27. Found: C, 43.54; H, 3.53%. The compound is soluble in CH₂Cl₂ and slightly soluble in acetone. ¹H NMR (δ, CD₂Cl₂, room temperature): 22.0 (br s, *w*_{1/2}=110 Hz, *o*-Ph of dppe), 10.4 (br s, *w*_{1/2}=25 Hz, *m*-Ph of dppe), 10.2 (br s, *w*_{1/2}=25 Hz, *p*-Ph of dppe), 7.2 (m, PPh₄), -21.8 (br s, *w*_{1/2}=210 Hz, CH₂). The presence of CH₂Cl₂ in the isolated solid was confirmed by ¹H NMR in acetone-d₆.

2.2. Reaction between MoI₃(dppe)(THF) and NaI. Synthesis of [Na(THF)₃][MoI₄(dppe)]

MoI₃(dppe)(THF) was prepared in situ from MoI₃(THF)₃ (450 mg, 0.64 mmol) and dppe (260 mg, 0.65 mmol) in 40 ml of THF. To the resulting solution was added NaI (105 mg, 0.70 mmol). After stirring for 30 min at room temperature, the color of the solution had become darker red but an NMR (CDCl₃) indicated that starting material was still present. Further monitoring indicated that the reaction was complete after 2 days. The solution was concentrated to ~10 ml, then cooled to -20 °C resulting in the formation of a red crystalline solid, which was filtered off and dried under vacuum. Yield 350 mg (42%). The compound is soluble in THF and acetone, insoluble in CH₂Cl₂. ¹H NMR (δ, acetone-d₆, room temperature): 21.1 (br s, *w*_{1/2}=120 Hz, *o*-Ph of dppe), 10.2 (br s, *w*_{1/2}=30 Hz, *m*-Ph of dppe), 10.0 (br s, *w*_{1/2}=~25 Hz, *p*-Ph of dppe), 3.62 (s, α-H of THF), 1.79 (s, β-H of THF), -22.5 (br s, *w*_{1/2}=220 Hz, CH₂). ¹H NMR (δ, THF-d₈, room temperature): 25.3 and 22.0 (br s, *w*_{1/2}=140 Hz, *o*-Ph of dppe), 12.1 and 10.3 (br s, *w*_{1/2}=25 Hz, *m*-Ph of dppe), 10.6 and 10.1 (br s, *w*_{1/2}=25 Hz, *p*-Ph of dppe), -10.5 and -22.1 (br s, *w*_{1/2}=180 Hz, CH₂). These properties are identical with those of the crystallographically characterized [Na(THF)₃][MoI₄(dppe)]·THF compound, obtained as described below. The compounds easily loses THF upon separation from the mother liquor.

2.3. Reaction of MoI₃(dppe)(THF) with Na⁺C₉H₇⁻. Crystallization of [Na(THF)₃][MoI₄(dppe)]·THF

MoI₃(dppe)(THF) was prepared in situ from MoI₃(THF)₃ (614 mg, 0.89 mmol) and dppe (353 mg,

0.89 mmol) in 40 ml of THF. To the resulting solution was added a THF solution of Na⁺C₉H₇⁻ (0.683 M, 1.30 ml, 0.89 mmol). After stirring for 3 days at room temperature, the red solution was evaporated to dryness. The residue was extracted with toluene (30 ml), then with CH₂Cl₂ (25 ml). A red residue remained still undissolved. This was redissolved in THF (25 ml) and the resulting solution was concentrated to ~10 ml. Diffusion of heptane and cooling to -20 °C afforded 261 mg of crude product, the NMR spectrum of which was identical with that of the material obtained from MoI₃(dppe)(THF) and NaI (see Section 2.2). Recrystallization from THF/Et₂O gave red single crystals which were used for the X-ray analysis. These immediately lost their X-ray diffraction capability unless they were mounted under mother liquor.

2.4. ¹H NMR investigation of MoI₃(dppe)(THF)

A CD₂Cl₂ solution of MoI₃(dppe)(THF) showed the following ¹H NMR resonances at room temperature when recorded immediately (δ): 90 (br s, *w*_{1/2}=450 Hz, α-H of THF), 27.5 and 23.0 (br s, *w*_{1/2}=220 Hz, *o*-Ph), 16.5 (br s, *w*_{1/2}=90 Hz, β-H of THF), 13.2 and 12.5 (br s, *w*_{1/2}=40 Hz, *p*-Ph), 10.9 and 10.0 (br s, *w*_{1/2}=35 Hz, *m*-Ph), -10.0 and -14.0 (br s, *w*_{1/2}=200 Hz, CH₂ of dppe). Soon after the dissolution of the compound in CD₂Cl₂, THF molecules were lost from the coordination sphere as indicated by the growth of the typical ¹H NMR resonances of free THF at δ 2.2 and 3.9. The THF loss from MoI₃(dppe)(THF) to afford an isolable [MoI₃(dppe)]_x compound has been previously reported [7].

2.5. X-ray crystallography for [Na(THF)₃]- [MoI₄(dppe)]·THF

A suitable crystal was mounted in a random orientation inside a glass capillary under mother liquor. Rotation photographs were used to locate reflections whose setting angles were then refined and used to determine the unit cell and orientation matrix for the crystal. Axial photographs confirmed axial lengths for the unit cell and mirror symmetry with respect to a single axis. Conditions for reflection (*h*0*l*: *h*+*l*=2*n* and 0*k*0: *k*=2*n*) were the only restrictions on reflection class and allowed the assignment of space group *P*2₁/*n*. The periodical monitoring of three intensity standards indicated no decay. The empirical absorption correction was based on ψ scans of 7 reflections at 10° intervals.

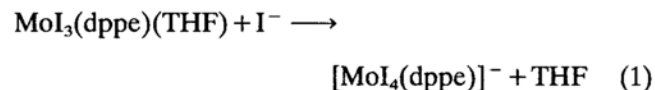
The structure was solved via direct methods and completed with difference Fourier syntheses. All non-hydrogen atoms were initially refined with anisotropic temperature factors. However, the carbon atoms of the three coordinated and one interstitial THF molecules

were highly thermally active and a few became 'non-positive definite', therefore they were eventually refined isotropically. Hydrogen atoms for the dppe ligands were included at calculated positions and assigned an isotropic thermal parameter $B = 1.2B$ (equivalent isotropic) for attached carbon atom and were used for structure factor calculations but not refined. Their position, however, was updated through the final cycles of refinement. The hydrogen atoms of the four THF molecules were not included.

Selected crystal data are collected in Table 1, positional and equivalent isotropic thermal parameters are listed in Table 2, and selected bond distances and angles are in Table 3.

3. Results and discussion

The *cis*-[MoI₄(dppe)]⁻ ion was formed according to Eq. (1) and isolated as the PPh₄⁺ and Na(THF)₃⁺ salts.



The sodium salt was also obtained by addition of indenylsodium to MoI₃(dppe)(THF) [2], intended to provide a synthesis of (C₉H₇)MoI₂(dppe). The free iodide ion generated by indenyl substitution is presumably competing with additional indenyl anion for replacement of the labile THF ligand. The structure of MoI₃(dppe)(THF) has a meridional octahedral geometry [2] and an NMR study of ligand substitution reactions at octahedral Mo(III) indicates a strong *trans* directing ability of phosphine ligands [8]. Thus, we propose the sequence of events shown in Scheme 1.

This reaction is complicated by other phenomena, such as reduction of the metal by the indenyl anion.

Table 1
Crystal data for [Na(THF)₃][MoI₄(dppe)]·THF

Formula	MoI ₄ P ₂ NaO ₄ C ₄₂ H ₅₆
Formula weight	1313.40
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.790(2)
<i>b</i> (Å)	16.512(7)
<i>c</i> (Å)	23.117(4)
β (°)	103.65(1)
<i>V</i> (Å ³)	4744(4)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.84
μ (Mo <i>K</i> α) (cm ⁻¹)	30.21
No. observed data ($F_o > 3\sigma(F_o)$)	4885
No. parameters refined	398
<i>R</i> ^a	0.039
<i>R</i> _w ^b	0.060

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

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

Table 2
Positional parameters and *B*_{eq} values for (THF)₃Na(μ-I)₃MoI(dppe)·THF

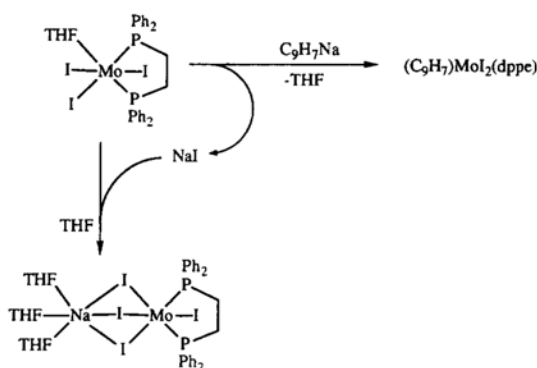
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
I(1)	0.07279(5)	0.05978(4)	0.20684(3)	4.65(3)
I(2)	0.14504(6)	0.05191(4)	0.38505(3)	5.68(3)
I(3)	0.37094(5)	-0.01352(5)	0.30134(3)	5.48(3)
I(4)	-0.04171(5)	-0.12283(4)	0.28743(3)	4.95(3)
Mo	0.16024(6)	-0.05595(5)	0.29353(3)	3.50(3)
P(1)	0.2308(2)	-0.1771(1)	0.3613(1)	3.9(1)
P(2)	0.1808(2)	-0.1576(2)	0.2134(1)	3.8(1)
Na	-0.1115(4)	0.0640(3)	0.2856(2)	6.9(2)
O(1)	-0.2114(8)	0.0348(6)	0.3551(5)	8.4(5)
O(2)	-0.2603(8)	0.0656(8)	0.2057(5)	11.6(7)
O(3)	-0.1177(8)	0.2013(6)	0.2898(5)	9.5(6)
C(1)	0.2246(8)	-0.2630(6)	0.3109(4)	4.7(4)
C(2)	0.2628(8)	-0.2396(6)	0.2550(4)	4.7(4)
C(10)	0.1638(8)	-0.2177(6)	0.4171(4)	4.4(4)
C(11)	0.096(1)	-0.1703(7)	0.4407(5)	6.1(6)
C(12)	0.048(1)	-0.2014(8)	0.4845(5)	6.6(6)
C(13)	0.068(1)	-0.2782(9)	0.5028(5)	6.6(6)
C(14)	0.137(1)	-0.3264(7)	0.4800(5)	6.2(6)
C(15)	0.1846(8)	-0.2951(6)	0.4381(4)	5.1(5)
C(20)	0.3664(7)	-0.1754(6)	0.4060(4)	4.3(4)
C(21)	0.3901(9)	-0.1188(8)	0.4497(5)	6.2(6)
C(22)	0.492(1)	-0.1182(8)	0.4905(6)	7.5(7)
C(23)	0.567(1)	-0.173(1)	0.4846(7)	7.9(7)
C(24)	0.541(1)	-0.230(1)	0.4410(8)	8.6(8)
C(25)	0.4434(8)	-0.2292(6)	0.4013(5)	5.7(5)
C(30)	0.2498(7)	-0.1343(6)	0.1545(4)	4.4(4)
C(31)	0.2782(8)	-0.0571(7)	0.1428(5)	5.4(5)
C(32)	0.329(1)	-0.0423(8)	0.0956(6)	6.6(6)
C(33)	0.348(1)	-0.107(1)	0.0611(5)	7.8(8)
C(34)	0.319(1)	-0.184(1)	0.0710(5)	7.0(7)
C(35)	0.2669(9)	-0.1982(8)	0.1167(5)	6.1(6)
C(40)	0.0589(7)	-0.2046(6)	0.1688(4)	4.0(4)
C(41)	-0.0125(8)	-0.1551(7)	0.1330(5)	5.4(5)
C(42)	-0.1041(9)	-0.1871(8)	0.0964(5)	6.2(6)
C(43)	-0.121(1)	-0.2694(8)	0.0962(6)	6.9(6)
C(44)	-0.047(1)	-0.3178(7)	0.1331(6)	8.0(7)
C(45)	0.041(1)	-0.2869(7)	0.1676(5)	5.9(5)
C(51)	-0.157(2)	0.031(1)	0.420(1)	12.9(6)
C(52)	-0.198(3)	-0.054(2)	0.433(1)	20(1)
C(53)	-0.293(2)	-0.072(2)	0.380(1)	18(1)
C(54)	-0.297(2)	-0.018(1)	0.335(1)	12.0(5)
C(55)	-0.264(2)	0.044(1)	0.146(1)	14.4(7)
C(56)	-0.346(4)	0.120(3)	0.118(2)	27(2)
C(57)	-0.407(3)	0.112(3)	0.156(2)	26(2)
C(58)	-0.355(2)	0.106(2)	0.212(1)	16.9(9)
C(59)	-0.178(2)	0.249(2)	0.318(1)	14.4(7)
C(60)	-0.145(2)	0.332(1)	0.3241(9)	12.1(5)
C(61)	-0.072(2)	0.339(1)	0.288(1)	12.8(6)
C(62)	-0.072(2)	0.264(2)	0.257(1)	16.5(8)
O(4)	0.061(2)	0.058(1)	0.028(1)	9.4(6)
C(63)	0.120(2)	0.028(2)	-0.007(1)	6.5(5)
C(64)	-0.004(6)	0.034(4)	0.021(3)	17(2)
C(65)	0.065(3)	-0.044(2)	-0.020(1)	7.4(7)

The formation of the Mo(II) complex (η^5 -C₉H₇)(η^3 -C₉H₇)Mo(dppe), which is optimized when three equivalents of C₉H₇Na are used, has been previously reported [9]. At the end of the reaction, the THF solvent is

Table 3
Selected bond distances (Å) and angles (°) for (THF)₃Na(μ-I)₃MoI(dppe)·THF

I1–Mo	2.804(1)	P1–C1	1.83(1)
I1–Na	3.301(5)	P1–C10	1.84(1)
I2–Mo	2.807(1)	P1–C20	1.80(1)
I2–Na	3.540(5)	P2–C2	1.84(1)
I3–Mo	2.749(1)	P2–C30	1.83(1)
I4–Mo	2.782(1)	P2–C40	1.827(9)
I4–Na	3.209(5)	Na–O1	2.33(1)
Mo–P1	2.569(3)	Na–O2	2.32(1)
Mo–P2	2.559(3)	Na–O3	2.27(1)
Mo–I1–Na	80.59(8)	C10–P1–C20	98.5(4)
Mo–I2–Na	76.39(8)	Mo–P2–C2	104.3(3)
Mo–I4–Na	82.59(9)	Mo–P2–C30	123.4(3)
I1–Mo–I2	91.11(4)	Mo–P2–C40	117.9(3)
I1–Mo–I3	95.32(3)	C2–P2–C30	103.2(4)
I1–Mo–I4	91.45(3)	C2–P2–C40	106.7(5)
I1–Mo–P1	171.80(7)	C30–P2–C40	99.6(4)
I1–Mo–P2	91.21(6)	I1–Na–I2	71.6(1)
I2–Mo–I3	91.72(3)	I1–Na–I4	75.8(1)
I2–Mo–I4	93.53(4)	I1–Na–O1	163.0(3)
I2–Mo–P1	96.41(7)	I1–Na–O2	96.9(3)
I2–Mo–P2	177.45(7)	I1–Na–O3	94.7(3)
I3–Mo–I4	171.35(4)	I2–Na–I4	74.0(1)
I3–Mo–P1	87.74(6)	I2–Na–O1	96.6(3)
I3–Mo–P2	87.02(6)	I2–Na–O2	168.2(3)
I4–Mo–P1	84.84(6)	I2–Na–O3	93.7(3)
I4–Mo–P2	87.46(6)	I4–Na–O1	89.3(3)
P1–Mo–P2	81.34(8)	I4–Na–O2	101.2(4)
Mo–P1–C1	105.1(3)	I4–Na–O3	166.3(3)
Mo–P1–C10	123.9(3)	O1–Na–O2	94.1(4)
Mo–P1–C20	119.4(3)	O1–Na–O3	98.4(4)
C1–P1–C10	102.0(4)	O2–Na–O3	89.5(5)
C1–P1–C20	105.6(5)		

E.s.d.s in the least significant figure are given in parentheses.



Scheme 1.

totally removed. Washing the residues with toluene and then CH₂Cl₂ removes all products except for red [Na(THF)₃][MoI₄(dppe)], which is then recrystallized from THF/Et₂O.

An X-ray structural study of the sodium salt reveals the geometry shown in Fig. 1 for the molecule. Overall, the geometry can be described as a face-shared bioctahedron, the shared triangular face being defined by the three bridging iodide ligands. The octahedral ge-

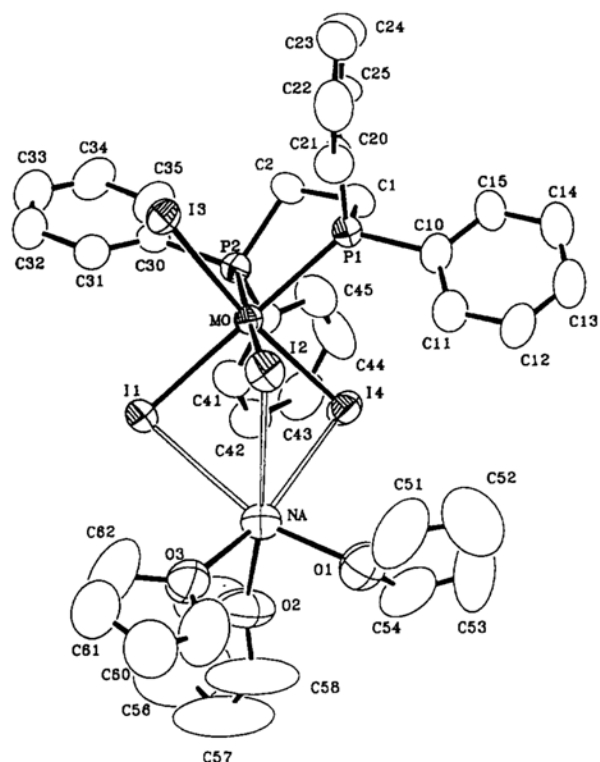


Fig. 1. An ORTEP view of the (THF)₃Na(μ-I)₃MoI(dppe) molecule with the atomic numbering scheme employed. Hydrogen atoms are omitted for clarity.

ometry around Na⁺ is completed by three THF molecules, while that around Mo³⁺ is completed by dppe and by an additional iodide ligand. The deviations from the octahedral geometry are smaller for the Mo center (angles between bonds to ligands located in relative *trans* positions are greater than 170°) than for the Na center (angles smaller than 170°). These smaller *trans* angles for the Na coordination geometry are caused by two factors: one is the larger than 90° angle for THF–Na–THF caused by the steric bulk of the THF ligands, the second is the smaller than 90° angle for I–Na–I caused by the repulsion between the two metal centers. A repulsion between the two metals is also clearly indicated by the larger Na–I–Mo angles with respect to the ideal value for a face-shared bioctahedron of 70.53° [10]. The assembly of this structure can best be imagined as an ionic interaction between the [Na(THF)₃]⁺ unit and the coordination compound [MoI₄(dppe)][−]. The structure of the analogous [MoBr₄(dppe)][−] complex has been described [11].

The bonding parameters around the Mo center are as one would expect. The terminal Mo–I bond (Mo–I3, 2.749(1) Å) is shorter than the bridging ones and, amongst the latter ones, the Mo–I bond *trans* to the terminal I is shorter (Mo–I4, 2.782(1) Å) than those *trans* to phosphorus donors (av. 2.806(2) Å), in accord with expected trends of *trans* influence. These distances should be compared with those reported for *trans*-

[MoI₄(PEt₂Ph)₂]⁻ (av. 2.786(3) Å) [5] and for *mer*-MoI₃(dppe)(THF) (av. 2.755(1) Å for Mo–I bonds *trans* to each other, 2.769(1) Å for the Mo–I bond *trans* to the phosphorus donor). The Mo–P distances are quite similar to those observed in [MoBr₄(dppe)]⁻ salts [11].

The coordination sphere around the sodium atom is unusual. It is generally found that, whenever hard donor molecules such as ethers are available, the sodium ion prefers to bind to these rather than to the iodide counterion, which then is found in the lattice as an isolated I⁻ ion interacting with the Na center only through long-range coulombic forces. Typical examples of these are a variety of [Na(crown)]⁺I⁻ salts [12]. There are rare examples in the literature of sodium–iodine interactions with the iodide ion being part of the coordination sphere of Na⁺. From a Cambridge Structural Database search, only the following structures were found (Na–I distances in parentheses): [N(CH₂CH₂OCH₃)₃]NaI (2.972(3) Å) [13], [N(CH₂CH₂OH)₃]NaI (3.286(2) Å) [14], NaI·{N-[(3-oxabutyl)methyl]aza-12-crown-4} (3.088(1) Å) [15], [Na(μ-I)·(CH₃OCH₂CH₂)₂O]_∞ (3.164(1) Å) [16], [Na(μ-I)·(Me₂NCH₂CH₂NMe₂)₂]_∞ (3.00(1) and 3.28(1) Å) [17], {Na(μ-I)[Me₂NCH₂CH₂N(Me)CH₂CH₂NMe₂]}₂ (av. 3.09(2) Å) [18] and Na₃(μ₃-I){Ni[μ₃-OSi(O^tBu)₃]}₃ (av. 3.08(1) Å) [19]. Of these, the first three exhibit terminal Na–I interactions and the rest all involve bridging Na₂(μ-I) or Na₃(μ₃-I) interactions. In each case, the sodium center is bonded to only one or at the most two iodide ligands and each iodide ligand is bonded only to sodium atoms. The compound reported here, therefore, appears to be the first one in which the I⁻ ligand bridges sodium with a transition metal and the first case of a sodium coordination environment with three iodine atoms. A related structure is [Na(THF)₃][W₂Cl₇(THF)₂] [20], where the sodium exhibits five-coordination with two chloride ions functioning as bridging ligands between Na and W. The Na–I distances in the title compound (3.301(5), 3.540(5) and 3.209(5) Å for the bonds to I(1), I(2) and I(4), respectively) are longer than any of those previously reported, possibly the result of the dispersion of the ionic interaction among the three Na–I bonds. In spite of this apparently weakened Na–I interactions, the sodium atoms prefers to bind to three I atoms rather than to more solvent THF molecules, probably for entropic reasons (chelate effect), since one could consider the [MoI₄(dppe)]⁻ anion as a tridentate (tripodal) ligand toward Na⁺.

The ¹H NMR spectrum of the [MoI₄(dppe)]⁻ ion in CD₂Cl₂ is shown in Fig. 2. The paramagnetic shift of the ¹H NMR resonances for phosphine ligands coordinated to Mo(III) has been investigated to some extent [8,21]. In particular, it has been found that aliphatic protons in an α position with respect to the phosphorus atom are shifted upfield, typically in the

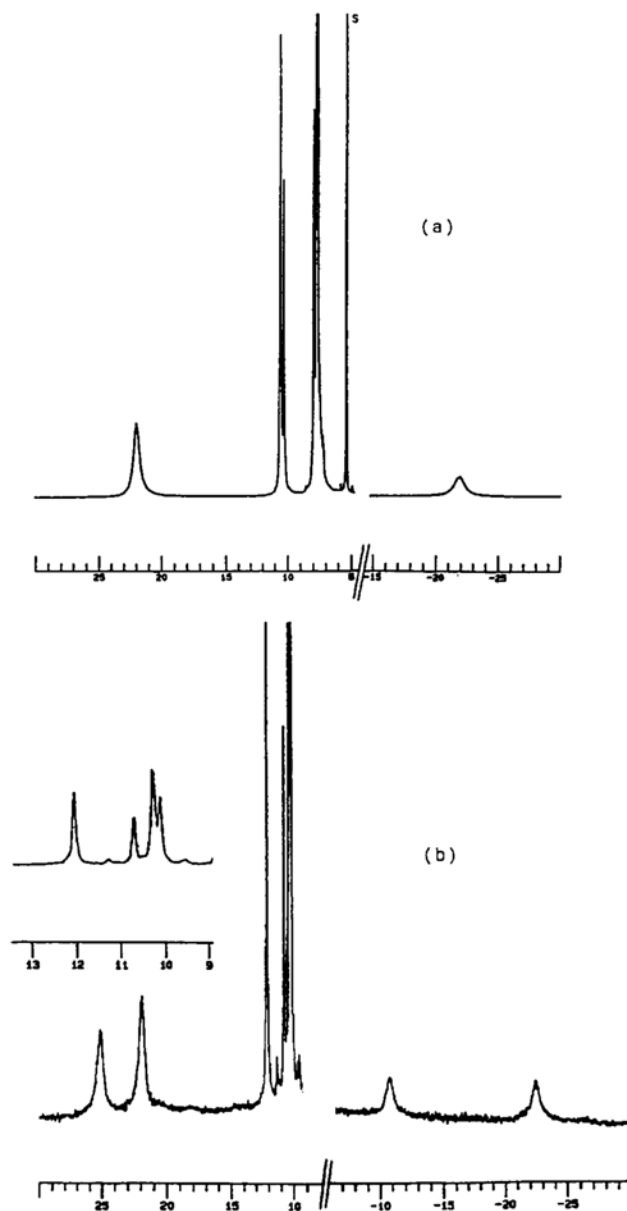


Fig. 2. Room temperature NMR spectra of [MoI₄(dppe)]⁻ salts: (a) PPh₄⁺[MoI₄(dppe)]⁻ in CD₂Cl₂ (the peak marked S is the solvent peak); (b) [Na(THF)₃][MoI₄(dppe)] in THF-d⁸.

δ -15 to -30 region at room temperature, whereas the protons of phenyl groups that are directly attached to the P atom are shifted downfield, between δ +7 and +20 depending on the phenyl carbon atom (*o*, *m*, *p*) to which they are bonded. The closer the phenyl H atoms are to the P atom, the broader and the more paramagnetically shifted its NMR resonance, although in some cases an *m/p* inversion in the chemical shift has been observed [21a]. Given these precedents, it is straightforward to assign, for the CD₂Cl₂ soluble PPh₄⁺ salt (Fig. 2(a)), the upfield shifted resonance at δ -22 to the dppe methylene protons and the downfield shifted resonances at δ 22, 10.4 and 10.2 to the phenyl *o*, *m* and *p* protons, respectively. The observations of only

one resonance for each type of proton is consistent with the high symmetry (C_{2v}) of the ion. For the $(\text{THF})_3\text{Na}(\mu\text{-I})_3\text{MoI}(\text{dppe})$ complex, the symmetry is lowered to C_s and therefore each resonance observed for the free $[\text{MoI}_4(\text{dppe})]^-$ ion should be split into two resonances of equal intensity. This is indeed the case when the spectrum is recorded in THF-d^8 solvent (Fig. 2(b)) and the same situation is found for the $\text{MoI}_3(\text{dppe})(\text{THF})$ precursor, for which an octahedral geometry with C_s symmetry has also been established by X-ray crystallography [2]. On the other hand, the ^1H NMR spectrum of $[\text{Na}(\text{THF})_3][\text{MoI}_4(\text{dppe})]$ in acetone- d^6 is identical to that observed for the corresponding PPh_4^+ salt in CD_2Cl_2 . This observation shows that the sodium salt retains the ion-paired solid state structure in THF solution, whereas in acetone it is either extensively dissociated, or the equilibrium between ion pair and separated ions is rapid, or the sodium cation rapidly migrates back and forth between the two possible I_3 triangular faces of the $[\text{MoI}_4(\text{dppe})]^-$ octahedron without ever completely dissociating from the anion, to give an overall dynamic C_{2v} geometry.

4. Supplementary material

Full tables of crystal data, bond distances and bond angles, tables of anisotropic thermal parameters, H-atom coordinates and calculated and observed structure factors (53 pages) have been deposited with the Crystallographic Data Centre.

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