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BIS(IMIDO) MOLYBDENUM(IV) COMPLEXES CONTAINING η^2-DIPHOSPHENE LIGANDS

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Abstract—Bis(imido) molybdenum complexes containing the diphosphene ligand $[2,4,6\text{-}(CF_3)_3C_6H_2]_2P_2$ ($Ar^FP = PAr^F$) have been prepared by displacement of the alkene ligands from $[Mo(N^tBu)_2(PMe_3)(CH_2 = CHMe)]$ and $[Mo(N\text{-}2,6\text{-}^iPr_2C_6H_3)_2(PMe_3)_2(C_2H_4)]$; the molecular structure of $[Mo(N^tBu)_2(PMe_3)(Ar^FP = PAr^F)]$ is reported. Copyright © 1996 Elsevier Science Ltd

The first diphosphene RP=PR (R = $2,4,6\text{-}^tBu_3C_6H_2$) was reported by Yoshifuji *et al.* in 1981,[1] and several compounds of this type have subsequently been described, including remarkably stable ones with strongly electron-withdrawing substituents such as $2,6\text{-}(CF_3)_2C_6H_3$[2,3] or $2,4,6\text{-}(CF_3)_3C_6H_2(Ar^F)$.[4–6] These have been shown to coordinate to suitable acceptors either in an η^1-fashion, *via* a lone pair on phosphorus, or in an η^2-mode, *via* the π system of the double bond. The vast majority of transition metal complexes containing diphosphene ligands, however, are in relatively low oxidation states.[7] Here we report the synthesis of some molybdenum complexes, which by virtue of two attendant imido groups, are maintained in the relatively high +4 oxidation state. The molecular structure of one of them provides the first structurally characterised example of a complex containing the $[2,4,6\text{-}(CF_3)_3C_6H_2]_2P_2$ ligand.

RESULTS AND DISCUSSION

Treatment of $[Mo(N^tBu)_2(PMe_3)(\eta^2\text{-}C_3H_6)]$ with one equivalent of the diphosphene, $Ar^FP{=}PAr^F$, in heptane leads to displacement of propene to give the η^2-diphosphene adduct $[Mo(N^tBu)_2(PMe_3)(Ar^FP{=}PAr^F)]$. The bis(arylimido)molybdenum complex, $[Mo(N\text{-}2,6\text{-}^iPr_2C_6H_3)_2(PMe_3)_2(C_2H_4)]$, reacts in a similar fashion with evolution of ethene and PMe_3 to give $[Mo(N\text{-}2,6\text{-}^iPr_2C_6H_3)_2(PMe_3)(Ar^FP{=}PAr^F)]$. Solution NMR data indicate closely related structures in which the diphosphene is η^2-bonded to the molybdenum centres: ^{31}P chemical shifts for the complexed diphosphenes lie in the range of other diphosphenes bound to transition metals.[7] The two ends of the diphosphenes are inequivalent according to ^{19}F NMR spectroscopy, implying that the P—P vector lies in the plane bisecting the two imido groups rather than within the plane that contains the two imido ligands.

Crystals of the *t*-butylimido derivative suitable for X-ray structure determination were grown from a saturated diethylether solution at 253 K. The crystallographic experimental details for this compound are given in Table 1, and its structure is illustrated in Fig. 1 (hydrogen and fluorine atoms are omitted for clarity.) Selected bond lengths and angles are listed in Table 2. The P(2)—P(3) distance of 2.160(2) Å is in the normal range for η^2-bonded diphosphenes, where most values lie between 2.11 and 2.19 Å.[7,8]

It is interesting to compare the structure of this compound with that of the bis-imidomolybdenum alkene complex[9] from which it is prepared. The bulkier diphosphene ligand forces the other bond angles around molybdenum to contract, such that

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Table 1. Crystal data and structure refinement

Chemical formula	$MoP_3N_2F_{18}C_{29}H_{31}$
Formula weight (M_r)	938.41
Temperature (K)	150(2)
λ, MoK_α (Å)	0.71073
Monochromator	Graphite
Crystal system	Triclinic
Space Group	$P\bar{1}$
a (Å)	12.265(6)
b (Å)	12.448(8)
c (Å)	14.760(7)
α (°)	66.45(4)
β (°)	88.01(4)
γ (°)	66.37(4)
V (Å^3)	1871(2)
Z	2
Absorption coefficient (μ) (cm^{-1})	0.593
F(000)	936
Crystal size (mm)	$0.80 \times 0.75 \times 0.40$
Crystal description	Prismatic
Crystal colour	Yellow
θ range for data collection	1.52 to 25.00°
Index ranges	$-14 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 0$, $-17 \leqslant l \leqslant 16$
Experiment device	Rigaku AFC6S
Experiment method	ω
Number of standard reflexions	3
Interval counts	150
Reflections collected	6583 [$R_{\mathrm{int}} = 0.015$]
Independent reflections	6583
Absorption correction	Empirical
$t_{\mathrm{min}}/t_{\mathrm{max}}$ transmission	0.868, 1.00
Refinement method[a]	Full-matrix least-squares on F^2
Data/restraints/parameters	6578/0/505
Goodness-of-fit on F^2	1.032
Final R indices [$I > 2\sigma(I)$]	$R^1 = 0.0303$, $wR_2 = 0.0799$
R indices (all data)	$R^1 = 0.0453$, $wR_2 = 0.1044$
Largest diff. peak and hole	0.893 and -0.633 e Å^{-3}
Anisotropic atoms	All non-H
Hydrogen atoms	Calculation[b]

[a] SHELXL-93.[11]

[b] Except four H-atoms on aromatic rings which were located from difference Fourier maps.

angle P(1)—Mo—N(1) is 101.9(1)° in the alkene and 95.99(9)° in the diphosphene complex, angle P(1)—Mo—N(2) contracts from 99.4(1)° to 95.58(9)° and angle N(1)—Mo—N(2) from 123.0(2)° to 115.90 (12)°. The molybdenum–nitrogen bonds are slightly shorter in the diphosphene complex (Mo—N(1) 1.757(3) Å, Mo—N(2) 1.763(3) Å) compared with its alkene analogue (Mo—N(1) 1.771(3) Å, Mo—N(2) 1.772(4) Å), whereas the bond from the PMe_3 ligand to the metal is slightly longer (2.475(2) Å *vs* 2.446(1) Å, respectively). These bond length variations are minor, however. The most significant differences lie in the angles at the imido nitrogens. In the ethene complex, the Mo—N—C angles are quite similar, 162.9(3) and 168.2(3)°, whereas in the diphosphene complex the corresponding angles are 177.1(2) and 154.1(2)°, the smaller angle possibly arising from unfavourable steric interactions between a trifluoromethyl substituent and the *t*-butyl group attached to N(2).

EXPERIMENTAL

All manipulations were carried out under dry nitrogen, either using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox. Solvents were refluxed over an appro-

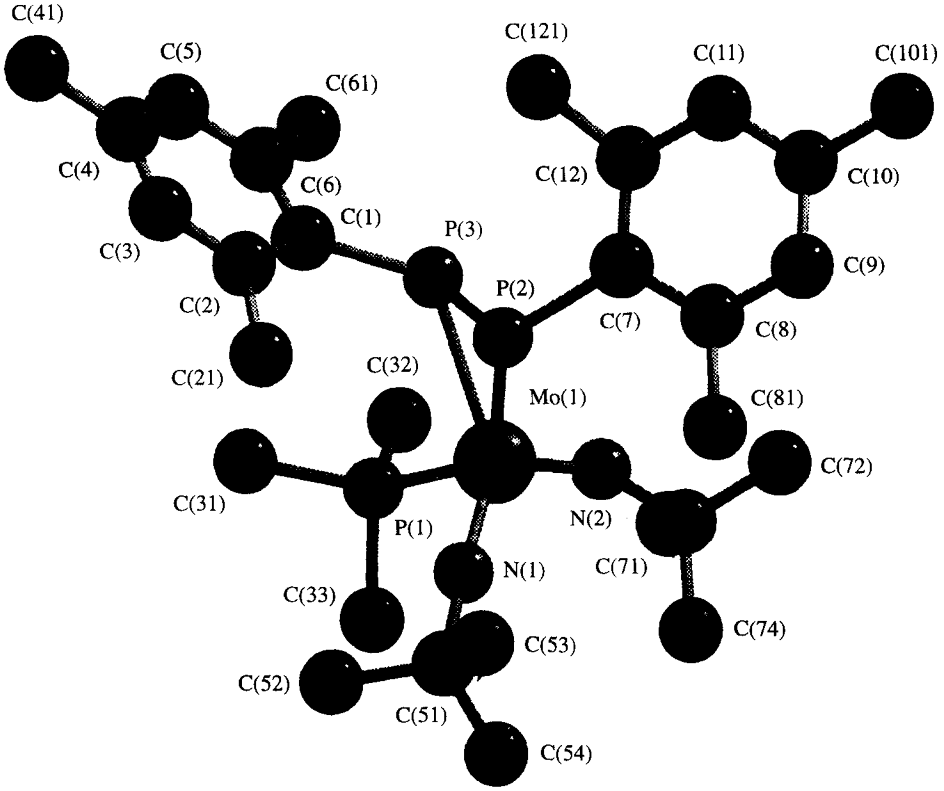

Fig. 1. The molecular structure of [Mo(N^{t}Bu)$_2$(PMe$_3$)(Ar^{F}P$=$PAr^F)] (fluorine atoms omitted for clarity).

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

Mo(1)—N(1)	1.757(3)	C(5)—C(6)	1.384(4)
Mo(1)—N(2)	1.763(3)	C(6)—C(61)	1.516(4)
Mo(1)—P(1)	2.475(2)	C(7)—C(12)	1.419(4)
Mo(1)—P(2)	2.538(2)	C(7)—C(8)	1.422(4)
Mo(1)—P(3)	2.588(2)	C(8)—C(9)	1.386(4)
P(2)—C(7)	1.862(3)	C(9)—C(10)	1.386(4)
P(2)—P(3)	2.160(2)	C(10)—C(11)	1.374(4)
P(3)—C(1)	1.878(3)	C(11)—C(12)	1.392(4)
N(2)—C(71)	1.467(4)	C(51)—C(54)	1.526(5)
N(1)—C(51)	1.461(4)	C(51)—C(52)	1.528(5)
C(1)—C(2)	1.416(4)	C(51)—C(53)	1.530(5)
C(1)—C(6)	1.436(4)	C(71)—C(74)	1.528(4)
C(2)—C(3)	1.389(4)	C(71)—C(72)	1.533(5)
C(3)—C(4)	1.378(5)	C(71)—C(73)	1.535(4)
C(4)—C(5)	1.385(5)		
N(1)—Mo(1)—N(2)	115.90(12)	P(3)—P(2)—Mo(1)	66.29(4)
N(1)—Mo(1)—P(1)	95.99(9)	C(1)—P(3)—P(2)	108.78(11)
N(2)—Mo(1)—P(1)	95.58(9)	C(1)—P(3)—Mo(1)	125.11(10)
N(1)—Mo(1)—P(2)	99.53(9)	P(2)—P(3)—Mo(1)	63.89(5)
N(2)—Mo(1)—P(2)	116.01(9)	C(71)—N(2)—Mo(1)	154.1(2)
P(1)—Mo(1)—P(2)	133.17(4)	C(51)—N(1)—Mo(1)	177.1(2)
N(1)—Mo(1)—P(3)	132.85(9)	C(2)—C(1)—C(6)	114.1(3)
N(2)—Mo(1)—P(3)	110.33(9)	C(2)—C(1)—P(3)	130.0(2)
P(1)—Mo(1)—P(3)	88.19(5)	C(6)—C(1)—P(3)	115.3(2)
P(2)—Mo(1)—P(3)	49.82(4)	C(12)—C(7)—C(8)	115.2(3)
C(7)—P(2)—P(3)	103.93(10)	C(12)—C(7)—P(2)	124.2(2)
C(7)—P(2)—Mo(1)	115.13(10)	C(8)—C(7)—P(2)	120.1(2)

priate drying agent, and distilled and degassed prior to use. Elemental analyses were carried out by the microanalytical services of the Chemistry Department at Durham. NMR spectra were recorded in C_6D_6(298 K) on a Varian VXR400S spectrometer at 400.0 MHz (^{1}H), 376.3 MHz (^{19}F), 161.9 MHz (^{31}P) and 100.6 MHz (^{13}C), and mass spectra on a VG7070E instrument.

The diphosphene $Ar^FP{=}PAr^F$ was synthesised as described previously.[6] The complexes $[Mo(N^tBu)_2(PMe_3)(\eta^2\text{-}C_3H_6)]$ and $[Mo(NAr)_2(PMe_3)_2(\eta^2\text{-}C_2H_4]$ (Ar = 2,6-$^iPr_2C_6H_3$) are readily accessed from $[Mo(NR)_2Cl_2(dme)]$ (R = ^{t}Bu[9], 2,6-$^iPr_2C_6H_3$[10]).

Synthesis of $[Mo(N^tBu)_2(PMe_3)(Ar^F{=}PAr^F)]$

$[Mo(N^tBu)_2PMe_3(\eta^2\text{-}C_3H_6)]$, (100 mg, 0.28 mmols) in heptane (15 cm^3) was added dropwise over 5 min to $Ar^FP{=}PAr^F$ (170 mg, 0.27 mmols) in heptane (15 cm^3) at room temperature. The pale brown solution was warmed to 333 K and stirred at this temperature for 3 days. During this time the solution changed colour to yellow–orange. The solvent was removed *in vacuo* and the remaining solid was extracted with diethyl ether (3 × 20 cm^3), which was reduced in volume to 20 cm^3. On cooling this solution to 195 K yellow–orange crystals were obtained. Yield: 150 mg, *ca* 58%. Found: C, 37.0; H, 3.4; N, 2.7. $C_{29}H_{31}N_2P_3F_{18}Mo$ requires C, 37.1; H, 3.3; N, 3.0%. ^{1}H NMR: δ 7.94 (s, 2H, Ar^FH), 7.80 (s, 2H, Ar^FH), 1.39 (s, 9H, $NCMe_3$), 0.94 (d, $^2J_{PH}$ 9.6 Hz, 9H, PMe_3), 0.74 (s, 9H, $NCMe_3$). ^{31}P NMR: 11.6 (s, PMe_3), −11.32 (sept, 1P), −11.38 (sept, 1P). ^{19}F NMR: −51.89 (t, $^4J_{PF}$ 35.3 Hz, 6F, *o*-CF_3), −53.67 (t, $^4J_{PF}$ 42.1 Hz, 6F, *o*-CF_3), −62.83 (s, 3F, *p*-CF_3), −62.95 (s, 3F, *p*-CF_3). ^{13}C NMR: 160.5 (m, broad, *ipso* Ar^F), 155.3 (*ipso* Ar^F), 139.15, 137.15 (qd, *p*-*C*-CF_3, $^2J_{CF}$ 29.90 Hz, $^4J_{PC}$ 10.66 Hz), 126.1 (*o*-*C*-CF_3),125.6 (*m*-Ar^F), 124.4, 124.1 (q, *o*-C-*C*F_3, $^1J_{CF}$ 30.88 Hz), 123.7, 121.4 (q, p-C-*C*F_3, $^1J_{PC}$ 30.88 Hz), 70.1 (s, $NCMe_3$), 69.2 (s, $NCMe_3$), 65.9 (Et_2O), 32.3 (q, N*C*Me_3), 31.5 (q, N*C*Me_3), 19.3 (d, PMe_3, $^2J_{PC}$ 31 Hz, $^1J_{CH}$ 124 Hz), 15.55 (s, Et_2O). MS (EI^+, *m/z*, ^{98}Mo): 940 [M^+]. IR (Nujol mull, CsI, cm^{-1}): 2722(w), 1619(s), 1564(s), 1282(m), 1175(d), 1126(d), 1071(s), 911(s), 828(w), 737(d), 685(s).

Synthesis of $[Mo(NAr)_2(PMe_3)(Ar^FP{=}PAr^F)]$

$[Mo(NAr)_2(PMe_3)_2(\eta^2\text{-}C_2H_4)]$ (135 mg, 0.24 mmols) in heptane (15 cm^3) was added dropwise over 5 min to $Ar^FP{=}PAr^F$ (153 mg, 0.24 mmols) in heptane (20 cm^3) at room temperature. The pale brown solution was warmed to 60°C and stirred at this temperature for 3 days. During this time the solution changed colour to orange. The solvent was removed *in vacuo* and the remaining solid was extracted with diethyl ether (3 × 20 cm^3). On cooling this solution to 195 K bright orange crystals were obtained. Yield: 210 mg, *ca* 76%. Found: C, 47.0; H, 4.2; N, 2.6. $C_{45}H_{47}N_2P_3F_{18}Mo$ requires C, 47.1; H, 4.1; N, 2.4%. ^{1}H NMR: δ 7.9 (s, 2H, Ar^FH), 7.7 (s, 2H, Ar^FH), 7.07–7.02 (m, 3H, *m,p*-C_6H_3), 6.85–6.80 (m, 3H, *m,p*-C_6H_3), 3.84 (sept, $^3J_{CH}$ 6.4 Hz, 2H, $CHMe_2$), 3.59 (sept, $^3J_{CH}$ 6.4 Hz, 2H, $CHMe_2$), 1.28 (d, 6H, $CHMe_3$), 1.16 (d, 6H, $CHMe_3$), 1.06 (d, 6H, $CHMe_3$), 1.01 (d, $^2J_{PH}$ 10 Hz, 9H, PMe_3), 0.59 (d, 6H, $CHMe_3$). ^{31}P NMR: 7.8 (s, 1P, PMe_3), 3.6 (broad, 2P). ^{19}F NMR: −53.14 (t, $^4J_{PF}$ 30.7 Hz, 6F, *o*-CF_3), −53.82 (t, $^4J_{PF}$ 36.5 Hz, 6F, *o*-CF_3), −62.9 (s, 3F, *p*-CF_3), −63.1 (s, 3F, *p*-CF_3). ^{13}C NMR: 153.7, 152.8 (*ipso* NAr), 147.1, 141.8 (*p*-NAr), 140.4 (unresolved multiplet, *p*-*C*-CF_3), 138.2, 137.8 (unresolved multiplet, *o*-*C*-CF_3), 129.2 (*m*-NAr), 126.8, 126.6 (*m*-Ar^F), 125.6 (*m*-NAr), 123.2, 122.8 (*s*, *o*-NAr), 28.59, 28.24 ($CHMe_2$), 24.6, 23.8, 23.7, 23.6 ($CHMe_2$), 16.25 (d, PMe_3, $^1J_{PC}$ 30 Hz). CF_3 groups and Ar^F *ipso*-C unresolved. IR (KBr pellet, cm^{-1}) 2870(s), 1620(s), 1566(s), 1439(d), 1364(s), 1279(s), 1190(s), 1145(s), 1076(s), 959(s), 911(s), 856(s), 800(s), 747(s), 685(s).

X-ray crystallography

A summary of the crystallographic data and experimental details is given in Table 1. Lists of atomic coordinates, bond lengths and angles and atomic displacement parameters have been deposited with the Cambridge Crystallographic Data Centre.

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