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An unusual dirhenium complex containing the bridging 6-(diphenylphosphino)-2-pyridonate ligand

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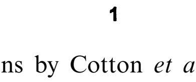
The diamagnetic dirhenium(II) complex $Re_2Cl_2(\mu\text{-pyphos})_2(\text{pyphosH})$ (**2**) is a product of the reactions between $(n\text{-}Bu_4N)_2Re_2Cl_8$, $Re_2(\mu\text{-}O_2CMe)_4Cl_2$ or *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ and 6-diphenylphosphino-2-pyridone (pyphosH) in refluxing acetonitrile. This formulation is based upon a single crystal X-ray structure determination and measurements of the magnetic susceptibility, EPR spectrum, electronic absorption spectrum and cyclic voltammetric properties of **2**. Unlike the known dimolybdenum(II) complex $Mo_2(\mu\text{-pyphos})_4$, which contains four N,O-bound pyphos ligands, all three bridging ligands in **2** are N,P-bound. The two anionic pyphos ligands are also involved in weaker 'axial' coordination of their O atoms to the dirhenium core. The dirhenium units are linked into dimers-of-dimers through strong intermolecular hydrogen bonds.

Introduction

The incorporation of metal–metal multiply bonded dimetal units that exhibit extensive redox chemistry[1] into mixed-metal low-dimensional materials has attracted recent interest in light of their potentially important magnetic, electronic and optical properties. Among the contributions in the field are those of Mashima *et al.*,[2] who reported the novel metal–metal bonded tetranuclear complexes $Mo_2M_2X_2(\text{pyphos})_4$ [M = Pd, Pt; X = halide; pyphos = 6-(diphenylphosphino)-2-pyridonate (**1**)], the formation of which involves the co-ordination of two M(II) units at the axial positions of $Mo_2(\mu\text{-pyphos})_4$[3] using the uncoordinated P donor sites, followed by the reduction of M(II) to M(I); this leads to the formation of Mo–M σ bonds and, consequently, M–Mo≡Mo–M units.[2] This group has also isolated the linear [Pd(0)][Mo(II)]$_2$[Pd(0)] complex $Mo_2Pd_2(\text{pyphos})_4$, which undergoes facile oxidative addition of dichloromethane to the Pd(0) centers,[4] as well as a closely related [Pt(II)][Cr(II)]$_2$[Pt(II)] complex in which there is a large increase in the Cr–Cr bond length over and above that expected for a Cr≣Cr bond.[5]



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Recent contributions by Cotton *et al.*[6] have demonstrated that the $M_2(\text{DPhIP})_4$ molecules [M = Cr, Mo; HDPhIP = 2,6-di(phenylimino)piperidine] can capture Cu(I) to form linear Cu ··· [M≣M] ··· Cu species in which the Cu(I) centers show a weak interaction with the M_2 unit. In a similar context, the neutral tridentate ligand 2,6-bis(diphenylphosphino)pyridine (bdppp) has been used to form the multiply bonded complexes $M_2Cl_4(\mu\text{-bdppp})_2$ (M = Mo, Re),[7] in which each bdppp ligand contains an uncoordinated phosphorus donor that has the potential to bind another metal center to form mixed-metal species.

In view of the structural similarities that so often exists between complexes that contain the $[Mo_2]^{4+}$ and $[Re_2]^{6+}$ cores, both of which possess the $\sigma^2\pi^4\delta^2$ ground state electronic configuration,[1] we have attempted to prepare a dirhenium complex of the pyphos ligand in the expectation that such a compound would be a useful precursor to low-dimensional dirhenium-containing materials and would provide an alternative to the other strategies we have recently used to incorporate dirhenium units into supramolecular assemblies.[8–10] To our surprise, we obtained an unsymmetrical dirhenium(II) complex of composition $Re_2Cl_2(\mu\text{-pyphos})_2(\mu\text{-pyphosH})$ (**2**) in which all three bridging ligands display an N,P bridging mode. This result stands in marked contrast to the structure of $Mo_2(\mu\text{-pyphos})_4$, where the four ligand bridges are N,O-bound and the P atoms are uncoordinated.[2]

Experimental

A. Starting materials

The dirhenium(III) complexes $(n\text{-}Bu_4N)_2Re_2Cl_8$,[11] *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$[12] and $Re_2(\mu\text{-}O_2CMe)_4Cl_2$,[13] and the ligand 6-diphenylphosphino-2-pyridone (pyphosH)[14] were all prepared by the literature methods. Solvents were obtained from commercial sources and were deoxygenated by purging with dinitrogen prior to use.

B. Synthesis of $Re_2Cl_2(\mu\text{-pyphos})_2(\mu\text{-pyphosH})$ (2)

A mixture of *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ (67 mg, 0.10 mmol) and 6-(diphenylphosphino)-2-pyridone (pyphosH; 112 mg, 0.40 mmol) was refluxed in 40 mL of acetonitrile for 3 days. The cooled reaction mixture was filtered and the insoluble mix of red crystals and red powder obtained was washed with acetonitrile (2 × 5 mL) and diethyl ether (2 × 5 mL); yield 53 mg (41%). Calc. for $C_{51}H_{40}Cl_2N_3O_3P_3Re_2$: C, 47.89; H, 3.15; found: C, 47.54; H, 3.46%.

When either $(n\text{-}Bu_4N)_2Re_2Cl_8$ or $Re_2(\mu\text{-}O_2CMe)_4Cl_2$ was used in place of *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$, the same product was obtained in yields of 23 and 31%, respectively. The identification of these products was based upon the similarity of their cyclic voltammetric properties and IR and NMR spectra to those of the sample prepared from *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$.

C. X-Ray crystallography

A crystal of composition $Re_2Cl_2(\mu\text{-pyphos})_2(\mu\text{-pyphosH})\cdot MeCN$ ($\mathbf{2}\cdot MeCN$) was selected from the mixture of red powder

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Table 1 Crystallographic data for the dirhenium complex **2**·MeCN

Formula	$C_{53}H_{43}Cl_2N_4O_3P_3Re_2$	V/Å^3		2407.1(2)
Formula weight	1320.19	D_c/g cm^{-3}		1.820
Crystal system	Triclinic	μ(Mo-Kα)/mm^{-1}		5.351
Space group	$P\bar{1}$ (no. 2)	Reflections	collected	25823
a/Å	11.7392(4)		independent	10901
b/Å	13.4032(5)		observed [$I > 2\sigma(I)$]	7925
c/Å	15.4780(6)	No. of variables		605
α/°	84.3933(15)	R_{int}		0.055
β/°	89.5143(14)	$R(F_o)$ ^{a}		0.039
γ/°	83.296(2)	$R_w(F_o^2)$ ^{b}		0.083
Z	2	GOF		0.985

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. ^{b} $R_w = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

and red crystals that was formed in the reaction between *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ and pyphosH in acetonitrile (see section B). The crystal was mounted on a glass fiber in a random orientation. The data collection was carried out at 150(±1) K with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer. Lorentz and polarization corrections were applied to the data set. The key crystallographic data are given in Table 1.

The structure was solved using the structure solution program PATTY in DIRDIF-99.[15] The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms bound to carbon were placed in calculated positions according to idealized geometries with C–H = 0.95 Å and U(H) = $1.3U_{eq}$(C). They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK[16] was applied. The final refinements were performed using the program SHELXL-97.[17]

The structure solution and refinement of the crystal of **2**·MeCN proceeded routinely, and all non-hydrogen atoms were refined with anisotropic thermal parameters. It became apparent during the course of the structure determination that there is a very close approach of pairs of equivalent dirhenium molecules, such that the intermolecular O ··· O distances between symmetry-related atoms [*i.e.* distances O(16)–O(36a) and O(36)–O(16a)] are very short [2.480(6) Å]. This indicated the presence of a strong intermolecular O–H ··· O hydrogen bond. Although this H atom [labeled as H(16)] could not be located in the difference map, it was added between O(16) and O(36a) [and between O(36)–O(16a)] at a O(16)–H(16) distance of 0.85 Å and with a O(16)–H(16)–O(36a) angle of 180°. The largest peak in the final difference Fourier map (2.31 e Å^{-3}) was located 2.155 Å from P(2) and 1.684 Å from C(212).

CCDC reference number 178308.

See http://www.rsc.org/suppdata/dt/b2/b200563h/ for crystallographic data in CIF or other electronic format.

D. Physical measurements

Infrared spectra were recorded from KBr pellets on a Perkin-Elmer 2000 FT-IR spectrometer. Electronic absorption spectra were recorded using a Cary 300 spectrophotometer, while ^{1}H and ^{31}P{^{1}H} NMR spectra were obtained on a Varian INOVA 300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. The ^{31}P{^{1}H} spectra were recorded at 121.6 MHz, with 85% H_3PO_4 as an external standard. X-Band EPR spectra were recorded at 150 K on a Bruker ESP 300 instrument. Electrochemical measurements were carried out using a BAS Inc. Model CV-27 instrument in conjunction with a BAS Model RXY recorder and were recorded on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at 25 °C and are uncorrected for junction potentials. Under our experimental conditions, $E_{1/2}$ = +0.47 V *vs.* Ag/AgCl for the ferrocenium/ferrocene couple. Elemental microanalyses were performed by Dr H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and discussion

The reactions of the three quadruply bonded dirhenium(III) complexes *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$, $(n\text{-}Bu_4N)_2Re_2Cl_8$ and $Re_2(\mu\text{-}O_2CMe)_4Cl_2$ with four equivalents of 6-(diphenylphosphino)-2-pyridone (pyphosH) in refluxing acetonitrile afforded the same red crystalline complex **2**. The single crystal X-ray structure determination of this product shows that it has retained a dirhenium unit with a short Re–Re bond [2.2693(3) Å]. ORTEP[18] representations of the structure are shown in Fig. 1 and 2 and the important intramolecular bond distances and bond angles are listed in Table 2. The crystals contain a molecule of acetonitrile solvent that is at a non-bonding distance to the dirhenium unit.

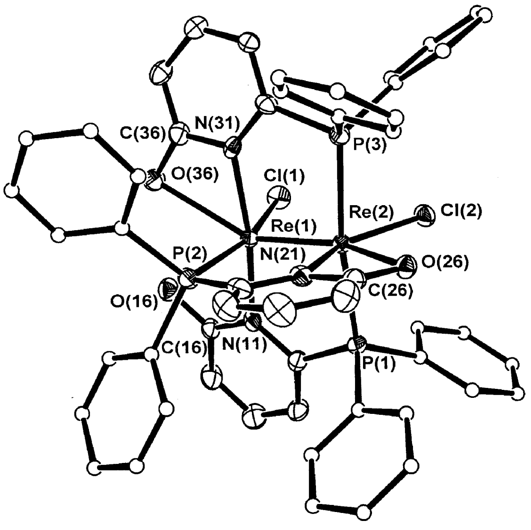

Fig. 1 ORTEP[18] representation of the structure of the dirhenium molecule present in **2**·MeCN. Thermal ellipsoids are drawn at the 50% probability level, except for the carbon atoms of the PPh_2 groups which are circles of arbitrary radius.

In contrast to the structure of $Mo_2(\mu\text{-pyphos})_4$, in which all four pyphos ligands are bound through their N and O donor atoms and the PPh_2 groups are uncoordinated,[2b,3] complex **2** contains three of these ligands that are bound in a bridging mode through their phosphine and pyridyl groups. In addition, two of the pyphos ligands are involved in significant interactions between their pyridonate O atoms and one of the Re atoms, while for the third pyphos ligand, the Re–O distance is indicative of an essentially non-bonding interaction (Fig. 1). The shortest Re–O distance is 2.422(4) Å [Re(2)–O(26)] and involves the pyphos ligand that is *trans* to a pair of Re–Cl bonds, while the distances Re(1)–O(16) and Re(1)–O(36), for the pair of *trans* head-to-head pyphos ligands, have values of

Table 2 Important bond distances (Å) and angles (°) for the dirhenium complex **2**·MeCN [a]

Re(1)–Re(2)	2.2693(3)	Re(2)–O(26)	2.422(4)
Re(1)–N(11)	2.139(4)	O(16)–C(16)	1.324(7)
Re(1)–N(31)	2.113(4)	O(26)–C(26)	1.283(7)
Re(1)–P(2)	2.3955(15)	O(36)–C(36)	1.292(7)
Re(1)–Cl(1)	2.3980(14)	N(11)–C(16)	1.342(8)
Re(1)–O(16)	2.979(4)	N(11)–C(12)	1.362(7)
Re(1)–O(36)	2.557(4)	N(21)–C(22)	1.352(7)
Re(2)–N(21)	2.068(5)	N(21)–C(26)	1.361(8)
Re(2)–P(1)	2.4047(14)	N(31)–C(32)	1.337(7)
Re(2)–P(3)	2.4602(14)	N(31)–C(36)	1.363(8)
Re(2)–Cl(2)	2.3718(14)		
N(31)–Re(1)–N(11)	165.58(19)	N(21)–Re(2)–P(1)	93.01(12)
N(31)–Re(1)–Re(2)	93.58(13)	Re(1)–Re(2)–P(1)	90.91(4)
N(11)–Re(1)–Re(2)	99.41(14)	Cl(2)–Re(2)–P(1)	86.99(5)
N(31)–Re(1)–P(2)	91.79(12)	N(21)–Re(2)–O(26)	57.74(17)
N(11)–Re(1)–P(2)	93.25(12)	Re(1)–Re(2)–O(26)	150.79(9)
Re(2)–Re(1)–P(2)	95.04(4)	Cl(2)–Re(2)–O(26)	93.18(10)
N(31)–Re(1)–Cl(1)	85.67(12)	P(1)–Re(2)–O(26)	91.16(9)
N(11)–Re(1)–Cl(1)	85.63(13)	N(21)–Re(2)–P(3)	91.32(12)
Re(2)–Re(1)–Cl(1)	101.59(4)	Re(1)–Re(2)–P(3)	95.07(4)
P(2)–Re(1)–Cl(1)	163.30(6)	Cl(2)–Re(2)–P(3)	86.21(5)
N(31)–Re(1)–O(36)	55.74(16)	P(1)–Re(2)–P(3)	172.42(5)
N(11)–Re(1)–O(36)	111.39(16)	O(26)–Re(2)–P(3)	85.89(9)
Re(2)–Re(1)–O(36)	149.19(6)	C(16)–N(11)–Re(1)	116.3(4)
P(2)–Re(1)–O(36)	84.20(10)	C(26)–N(21)–Re(2)	102.1(4)
Cl(1)–Re(1)–O(36)	80.73(10)	C(36)–N(31)–Re(1)	104.3(4)
N(31)–Re(1)–O(16)	117.16(15)	C(16)–O(16)–Re(1)	77.5(3)
N(11)–Re(1)–O(16)	49.34(15)	C(26)–O(26)–Re(2)	88.1(4)
Re(2)–Re(1)–O(16)	148.59(8)	C(36)–O(36)–Re(1)	86.0(3)
P(2)–Re(1)–O(16)	90.52(9)	O(16)–C(16)–N(11)	116.6(5)
Cl(1)–Re(1)–O(16)	76.10(9)	O(16)–C(16)–C(15)	122.2(6)
O(36)–Re(1)–O(16)	62.11(11)	O(26)–C(26)–N(21)	111.8(5)
N(21)–Re(2)–Re(1)	93.06(14)	O(26)–C(26)–C(25)	129.5(6)
N(21)–Re(2)–Cl(2)	150.92(15)	O(36)–C(36)–N(31)	113.3(5)
Re(1)–Re(2)–Cl(2)	116.02(4)	O(36)–C(36)–C(35)	128.0(6)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

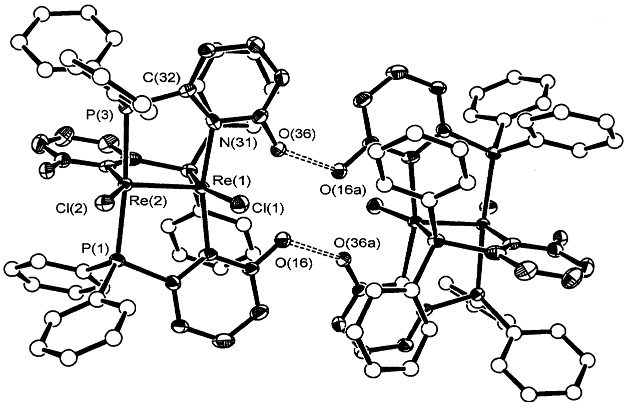

Fig. 2 ORTEP[18] representation of the structure of the dirhenium complex $Re_2Cl_2(\mu\text{-pyphos})_2(\mu\text{-pyphosH})$ showing how pairs of these molecules are linked into dimers-of-dimers by intermolecular H-bonds. Thermal ellipsoids are drawn at the 50% probability level, except for the carbon atoms of the PPh_2 groups which are circles of arbitrary radius.

2.557(4) and 2.979(4) Å, respectively. This disparity in Re–O distances, along with the recognition that if **2** is formulated as $Re_2Cl_2(\mu\text{-pyphos})_3$ it would contain a paramagnetic $[Re_2]^{5+}$ core, led us to investigate its magnetic and spectroscopic properties in order to differentiate between this formulation and the alternative, $Re_2Cl_2(\mu\text{-pyphos})_2(\mu\text{-pyphosH})$, which would be a diamagnetic dirhenium(ɪɪ) complex.

A magnetic susceptibility measurement on **2** established it to be diamagnetic. In addition, ESR spectral measurements (at 150 K) on both solid samples and a CH_2Cl_2–toluene glass showed the absence of the characteristic and complex signal that is typical of paramagnetic dirhenium(ɪɪɪ,ɪɪ) complexes that contain mixed halide/phosphine ligand sets.[19] Furthermore, the electronic absorption spectrum of a solution of **2** in dichloromethane shows absorptions at 432 (ε = 4800), 519 (10,200), 610sh (~3200) and 720sh nm (~700 $M^{-1}\ cm^{-1}$), but no absorption was observed in the region between 1000 and 2500 nm for a sample of **2** as a Nujol mull. The $\delta \longrightarrow \delta^*$ transition of paramagnetic dirhenium(ɪɪɪ,ɪɪ) complexes is located at ~1400 nm,[19–21] and its absence in the case of **2** favors the formulation of this complex as a dirhenium(ɪɪ,ɪɪ) species.

A cyclic voltammogram of a solution of **2** in 0.1 M $n\text{-}Bu_4NPF_6$–CH_2Cl_2 shows two reversible processes, with $E_{1/2}$ values of +1.00 and +0.22 V *vs.* Ag/AgCl, that correspond to two one-electron oxidations ($[Re_2]^{6+}/[Re_2]^{5+}$ and $[Re_2]^{5+}/[Re_2]^{4+}$) of the bulk complex; this behavior is typical of dirhenium(ɪɪ) complexes that have phosphine-containing bridging ligands. A good example is $Re_2Cl_3(\mu\text{-}Ph_2Ppy)_2[\mu\text{-}Ph(C_6H_4)Ppy]$, a complex that contains two 2-(diphenylphosphino)pyridine ligands *trans* to one another and a tridentate Ph_2Ppy ligand that has undergone orthometalation at the dirhenium core.[22] This complex has $E_{1/2}$ values of +1.06 and +0.24 V *vs.* SCE, behavior that is very similar to that observed for **2**. The first of the oxidations of **2** is accessible chemically using $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ as the one-electron oxidant.[23] The addition of one equivalent of this reagent to a solution of **2** in CH_2Cl_2 converts the red-colored complex to green $[\mathbf{2}]^+$, which has the same CV as that of **2**. This change can be followed by ^1H NMR spectroscopy (*vide infra*) but we have been unable to isolate pure samples of $[\mathbf{2}]PF_6$.

Although we could not obtain a satisfactory ^{31}P NMR spectrum of **2** because of its poor solubility in CD_2Cl_2 and other solvents, we were able to obtain a ^1H NMR spectrum in CD_2Cl_2 (and $CDCl_3$). In addition to the Ph resonances of the Ph_2P groups at δ +7.86, +7.45 and +7.35, weak, broad pyridyl ring resonances were observed at δ ~+6.4, ~+5.95 and ~+5.3. Upon addition of one equivalent of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ to this solution, the spectrum changes completely and is replaced by broad resonances at δ +9.58, +9.19, +8.,55, +8.18 and +7.71, along with a resonance for ferrocene (δ +4.33) that is formed following oxidation of **2** to $\mathbf{2}^+$ and the concomitant reduction of ferrocenium. These observations confirm that the process at +0.22 V corresponds to the $[Re_2]^{5+}/[Re_2]^{4+}$ couple and that **2** is a compound of dirhenium(ɪɪ,ɪɪ) and not dirhenium(ɪɪɪ,ɪɪ).

Based upon the foregoing evidence, we formulate **2** as $Re_2Cl_2(\mu\text{-pyphos})_2(\mu\text{-pyphosH})$. The question that now remains concerns the location of the extra hydrogen atom and, therefore, which of the three bridging ligands is actually pyphosH. The obvious candidate is the one in which the O atom is not at a bonding distance to an Re atom, *i.e.* O(16). The C–O distance for this O atom is a little longer than the C–O distances for the other bridging ligands [*i.e.* 1.324(7) Å *versus* 1.283(7) and 1.292(7) Å]. Furthermore, the intermolecular distance between atoms O(16) and O(36a) in adjacent symmetry-related molecules is 2.480(6) Å, which indicates that a strong *intermolecular* H-bond O(16)–H ··· O(36a) is present in the solid state. Accordingly, compound **2** exists as a dimer-of-dimers, as shown by the ORTEP representation of the structure in Fig. 2.

Concluding remarks

Previous work has established that the reactions of 2-hydroxypyridine and 2-mercaptopyridine ligands with dirhenium(ɪɪɪ) complexes afford complexes in which the dirhenium core is not reduced and in which these ligands assume their commonly encountered anionic N,O and N,S bridging modes.[24–27] In the present study, the use of a phosphine-substituted 2-hydroxypyridine ligand, *viz.*, the 6-(diphenylphosphino)-2-pyridonate ligand (pyphosH), leads to a 2-electron reduction of the dirhenium core and the formation of a complex in which the ligand adopts a dominant N,P bridging mode. The mechanisms for this type of reduction of dirhenium halide complexes by phosphine ligands and the solvent dependence of such reactions have been addressed previously by Cotton and coworkers.[28] The structure determination of $Re_2Cl_2(\mu\text{-pyphos})_2$-($\mu$-pyphosH) shows that the three pyphos/pyphosH ligands display markedly different degrees of interaction of their O atoms with the Re centers. This complex is structurally quite different from $Mo_2(\mu\text{-pyphos})_4$[2,3] and, therefore, unlikely to be useful in synthesizing mixed-metal assemblies, as has been shown to be the case with this dimolybdenum(II) complex.[2–5,29]

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References

1 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Oxford University Press, Oxford, 2nd edn., 1993.
2 (*a*) K. Mashima, H. Nakano and A. Nakamura, *J. Am. Chem. Soc.*, 1993, **115**, 11632; (*b*) K. Mashima, H. Nakano and A. Nakamura, *J. Am. Chem. Soc.*, 1996, **118**, 9083.
3 K. Mashima, H. Nakano, T. Mori, H. Takaya and A. Nakamura, *Chem. Lett.*, 1992, 185.
4 K. Mashima, A. Fukumoto, H. Nakano, Y. Kaneda, K. Tani and A. Nakamura, *J. Am. Chem. Soc.*, 1998, **120**, 12151.
5 K. Mashima, M. Tanaka, K. Tani, A. Nakamura, S. Takeda, W. Mori and K. Yamaguchi, *J. Am. Chem. Soc.*, 1997, **119**, 4307.
6 F. A. Cotton, C. A. Murillo, L. E. Roy and H.-C. Zhou, *Inorg. Chem.*, 2000, **39**, 1743.
7 F. A. Cotton, E. V. Dikarev, G. T. Jordan IV, C. A. Murillo and M. A. Petrukhina, *Inorg. Chem.*, 1998, **37**, 4611.
8 (*a*) S.-M. Kuang, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 2000, **39**, 2968; (*b*) S.-M. Kuang, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 2001, **40**, 5682.
9 J. K. Bera, P. Angaridis, F. A. Cotton, M. A. Petrukhina, P. E. Fanwick and R. A. Walton, *J. Am. Chem. Soc.*, 2001, **123**, 1515.
10 (*a*) S.-M. Kuang, P. E. Fanwick and R. A. Walton, *Inorg. Chem. Commun.*, 2001, **4**, 745; (*b*) S.-M. Kuang, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 2002, **41**, 405; (*c*) S.-M. Kuang, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 2002, **41**, 1036.
11 (*a*) T. J. Barder and R. A. Walton, *Inorg. Chem.*, 1982, **21**, 2510; (*b*) T. Barder and R. A. Walton, *Inorg. Synth.*, 1985, **23**, 116.
12 A. R. Chakravarty, F. A. Cotton, A. R. Cutler and R. A. Walton, *Inorg. Chem.*, 1986, **25**, 3619.
13 F. A. Cotton, C. Oldham and W. R. Robinson, *Inorg. Chem.*, 1966, **5**, 1798.
14 C. R. Newkome and D. C. Hager, *J. Org. Chem.*, 1978, **43**, 947.
15 P. T. Beurskens, G. Beurskens, R. deGelder, S. Garcia-Granda, R. O. Gould, R. Israel and J. M. M. Smits, The DIRDIF-99 Program System, Technical Report of the Crystallography Laboratory, University of Nijmegan, The Netherlands, 1998.
16 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1996, **276**, 307.
17 G. M. Sheldrick, SHELXL-97, A Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
18 C. K. Johnson, *ORTEP II, Report ORNL-5138*, Oak Ridge National Laboratory, TN, USA, 1976.
19 P. Brant, D. J. Salmon and R. A. Walton, *J. Am. Chem. Soc.*, 1978, **100**, 4424.
20 J. R. Ebner and R. A. Walton, *Inorg. Chim. Acta*, 1975, **14**, L45.
21 B. E. Bursten, F. A. Cotton, P. E. Fanwick, G. G. Stanley and R. A. Walton, *J. Am. Chem. Soc.*, 1983, **105**, 2606.
22 T. J. Barder, F. A. Cotton, G. L. Powell, S. M. Tetrick and R. A. Walton, *J. Am. Chem. Soc.*, 1984, **106**, 1323.
23 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.
24 F. A. Cotton and L. D. Gage, *Inorg. Chem.*, 1979, **18**, 1716.
25 A. R. Cutler and R. A. Walton, *Inorg. Chim. Acta*, 1985, **105**, 219.
26 A. R. Cutler, S. M. V. Esjornson, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 1988, **27**, 287.
27 R. M. Tylicki, W. Wu, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 1995, **34**, 988.
28 (*a*) P. Angaridis, F. A. Cotton, E. V. Dikarev and M. A. Petrukhina, *Polyhedron*, 2001, **20**, 755; (*b*) F. A. Cotton, E. V. Dikarev and M. A. Petrukhina, *Inorg. Chem.*, 1999, **38**, 3384.
29 K. Mashima, Y. Kaneda, A. Fukumoto, M. Tanaka, K. Tani, H. Nakano and A. Nakamura, *Inorg. Chim. Acta*, 1998, **270**, 459.