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FULL PAPER

Molybdenum and tungsten mono-isodiazene complexes with alkyl ligands as ring-opening metathesis polymerisation procatalysts. Crystal and molecular structures of [Mo($CH_2CMe_2Ph)_3$-($NNPh_2)(OC_6F_5)$], [W($CH_2SiMe_3)_3(NNPh_2)(OC_6F_5)$] and [$WCl_2(NNPh_2)(OC_6F_5)_2$(thf)]

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Reaction of [$M(NNPh_2)Cl_4$] with RMgCl followed by addition of pentafluorophenol afforded the tris-alkyl complexes [$MoR_3(NNPh_2)(OC_6F_5)$] [M = Mo, R = CH_2CMe_2Ph **1**; M = W, R = CH_2SiMe_3 **2**] in moderate yields. At *ca.* 80 °C in chlorobenzene **1** and **2** are active for the ring-opening metathesis polymerisation of norbornene; intermediate alkylidene complexes are not observed. The crystal structures of **1** and **2** have been determined; the metal centres adopt trigonal bipyramidal geometries in which the isodiazene and pentafluorophenoxide groups are apical. The crystal structure of [$WCl_2(NNPh_2)(OC_6F_5)_2$(thf)] **3** is also reported.

The role of 'spectator' ligands such as oxo or organoimido groups in stabilising olefin metathesis catalysts is well established. Imidoalkylidene complexes of the form [Mo(NAr)-($CHCMe_2Ph)(OR)_2$] [Ar = 2,6-$^iPr_2C_6H_3$; R = OBu^t, $OC(CF_3)$-Me_2 or $OC(CF_3)_2Me$] developed by Schrock and co-workers[1] are especially suited to the controlled polymerisation of a variety of norbornene and norbornadiene monomers. However, these four-co-ordinate imidoalkylidene initiators are quite thermally sensitive, leading to difficulties with storage and widespread applicability above ambient temperature.

We became interested in exploring the effect of replacing the imido ligands in the above systems by isodiazene groups, since in many cases isodiazene complexes are more thermally robust than their imido analogues. In separate studies, we have investigated the ring-opening metathesis polymerisation (ROMP) activity of nitride, isodiazene and diazenide procatalysts and have shown the first examples of such activity for these complexes.[2] Our previous attempts to prepare a new family of catalysts based on the bis(isodiazene) $Mo(NNPh_2)_2$ core have to-date met with little success.[3] However, in the case of the mono(isodiazene) $M(NNPh_2)$ systems, we believed that the higher formal oxidation state of the metal would facilitate alkylation. We now report the first examples of simple isodiazene complexes of the Group 6 metals with alkyl co-ligands which can be used to generate *in situ* active ROMP catalysts. The synthetic approach depends upon alkylation, followed by treatment with a Brønsted acid source, *viz.* C_6F_5OH, a methodology that has successfully been exploited to access metathesis-active imidoalkylidene complexes.[4]

Results and discussion

Attempts to alkylate [$M(NNPh_2)Cl_4$] (M = Mo or W) with neophyllithium, $PhMe_2CCH_2Li$ (>3 equivalents), afforded mixtures of products that could not be purified. However, the reaction of [$Mo(NNPh_2)Cl_4$][5] with neophylmagnesium chloride (>3 equivalents) in diethyl ether followed by addition of pentafluorophenol readily afforded on work-up multigram quantities of [$Mo(CH_2CMe_2Ph)_3(NNPh_2)(OC_6F_5)$] **1** as an air-stable orange-red crystalline solid in *ca.* 40% yield. Crystals of **1** suitable for an X-ray analysis were grown from pentane at 0 °C; a representation of the molecular structure is shown in Fig. 1. Selected bond lengths and angles appear in Table 1.

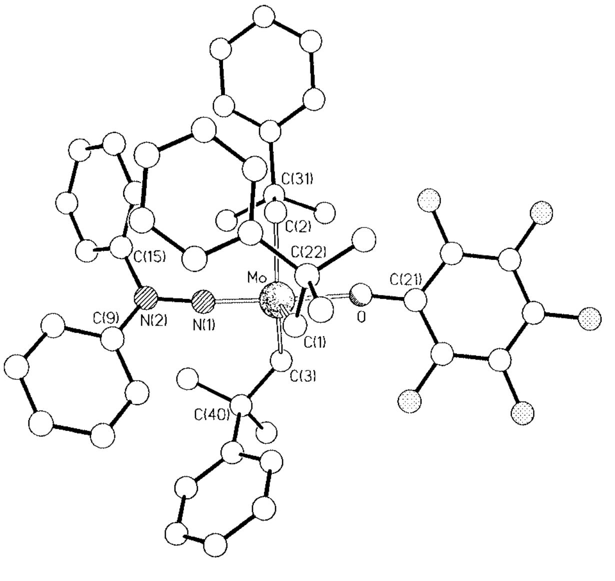

Fig. 1 View of the molecular structure of complex **1** (hydrogen atoms omitted for clarity in all Figures).

The molecular geometry is trigonal bipyramidal with the isodiazene and pentafluorophenoxide ligands axial [N(1)–Mo–O 177.31(9)°]. For the isodiazene ligand the N–N distance [N(1)–N(2) 1.333(4) Å], the Mo–N distance [1.746(2) Å] and the Mo–N(1)–N(2) angle [174.5(2)°] lie within the range found for other monoisodiazene complexes.[6] The equatorial neophyl groups are orientated in a "manx-like" arrangement with Mo–C bond lengths in the range 2.126(3) to 2.152(3) Å and inter-ligand C–Mo–C angles between 118.68(12) and 120.1(1)°. The associated Mo–C–C angles range between 120.2(2) and 130.5(2)°, the largest angle being associated with the shortest Mo–C

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Mo–O	2.011(2)	Mo–N(1)	1.746(2)
Mo–C(1)	2.152(3)	Mo–C(2)	2.144(3)
Mo–C(3)	2.126(3)	N(1)–N(2)	1.333(4)
N(1)–Mo–O	177.31(9)	N(1)–Mo–C(3)	97.2(1)
O–Mo–C(3)	85.5(1)	N(1)–Mo–C(2)	92.6(1)
O–Mo–C(2)	85.9(1)	C(3)–Mo–C(2)	118.7(1)
N(1)–Mo–C(1)	92.7(1)	O–Mo–C(1)	86.1(1)
C(3)–Mo–C(1)	120.1(1)	C(2)–Mo–C(1)	119.6(1)
C(21)–O–Mo	167.8(2)	N(2)–N(1)–Mo	174.5(2)
C(22)–C(1)–Mo	120.2(2)	C(31)–C(2)–Mo	122.9(2)
C(40)–C(3)–Mo	130.5(2)		

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

W–O	2.011(5)	W–N(1)	1.741(6)
W–C(1)	2.095(8)	W–C(2)	2.091(7)
W–C(3)	2.117(7)	N(1)–N(2)	1.337(8)
N(1)–W–O	177.3(3)	N(1)–W–C(2)	95.2(3)
O–W–C(2)	84.0(3)	N(1)–W–C(1)	94.6(3)
O–W–C(1)	88.0(3)	C(2)–W–C(1)	115.1(3)
N(1)–W–C(3)	94.3(3)	O–W–C(3)	83.9(3)
C(2)–W–C(3)	119.8(3)	C(1)–W–C(3)	123.2(3)
C(16)–O–W	157.3(5)	N(2)–N(1)–W	174.8(5)
Si(1)–C(1)–W	124.5(4)	Si(2)–C(2)–W	120.5(4)
Si(3)–C(3)–W	116.5(3)		

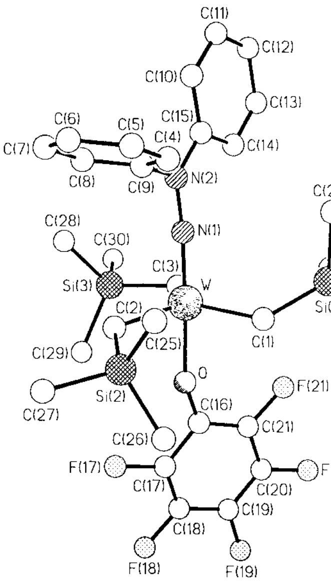

Fig. 2 View of the molecular structure of complex **2**.

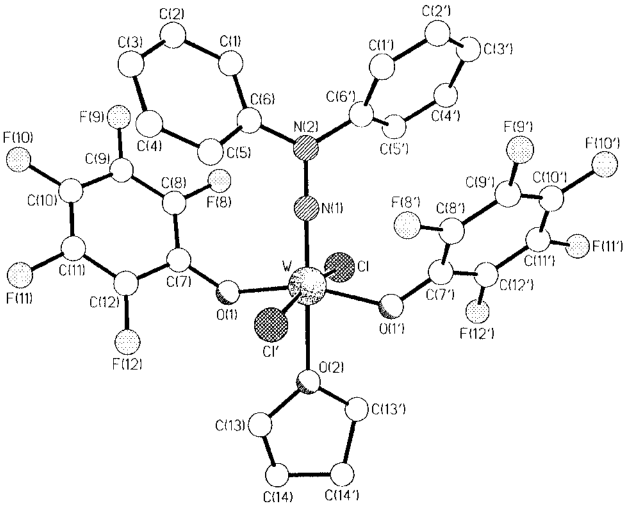

Fig. 3 View of the molecular structure of complex **3**.

distance. Conformational stabilisation is, in part, achieved by a C–H···π contact of 2.60 Å between one of the *ortho* isodiazene hydrogen atoms and the C(1) neophyl ring. The only intermolecular feature of note is a partial stacking of C_i related pentafluorophenoxy rings where F(19) in one ring overlays C(20) [attached to F(20)] of the other at an internuclear distance of only 3.11 Å and at 3.07 Å from the plane of the ring. The neophyl groups are located in *cis* positions which should facilitate α-H abstraction *via* alkane elimination. Solution ^{1}H NMR data at ambient temperature are consistent with retention of this structure. However, attempts to observe an alkylidene intermediate by NMR upon warming the complex were unsuccessful, only decomposition products being observed. Treatment of **1** with 100 equivalents of norbornene in chlorobenzene (80 °C, 12 h) yielded ring-opened polynorbornene in *ca.* 50% isolated yield and with *ca.* 70% *cis* double bonds as indicated by ^{13}C NMR spectroscopy. Gel permeation chromatography (GPC) data on the polymer gave a number average molecular weight (M_n) of 55 100 [calc. 9416] and a PDI (polymer distribution index) of 1.82. The M_n of the polymer and comparatively narrow molecular weight distribution are consistent with efficient catalyst formation.

A similar reaction of [$WCl_4(NNPh_2)$] with trimethylsilylmethylmagnesium chloride, Me_3SiCH_2MgCl, gave, following the addition of C_6F_5OH, the golden-yellow crystalline complex [$W(CH_2SiMe_3)_3(NNPh_2)(OC_6F_5)$] **2** in *ca.* 30% yield. The molecular structure of **2** is depicted in Fig. 2; selected bond lengths and angles are given in Table 2. The gross structure is very similar to that of **1** with the tungsten having trigonal bipyramidal geometry.

As in complex **1**, the alkyl groups are equatorial and orientated in a "manx-like" arrangement with W–C distances in the range 2.091(7) to 2.117(7) Å and interligand C–W–C angles between 115.1(3) and 123.2(3)°. The associated W–C–Si angles range between 116.5(3) and 124.5(4)°. The isodiazene ligand is again linear [174.8(5)°] with a W–N bond distance of 1.741(6) Å and an N–N distance of 1.337(8) Å. Here, in **2**, the W–O–C_6F_5 angle is noticeably bent at 157.3(5)°, *cf.* 167.8(2)° for **1**, the reason for which is not immediately apparent. The packing of the molecules is very different from that in **1** with here the closest intermolecular contacts being T-type aromatic edge to face interactions between C_i related pairs of diphenylisodiazene ring systems, the centroid–centroid distance being 5.15 Å. Reaction as for **1** with norbornene afforded polynorbornene but only in 10% yield. Polymer characterising data were consistent with *ca.* 45% *cis*-configurated double bonds, a molecular weight (M_n) of 560 000 and a molecular weight distribution of 2.77.

Surprisingly, attempts at an analogous reaction with benzylmagnesium chloride afforded only [$WCl_2(NNPh_2)(OC_6F_5)_2$(thf)] **3**. The reasons for the failure of benzylmagnesium chloride to react at this stage are not clear; it is possible however that an unisolable bis(benzyl) intermediate reacts *in situ* with pentafluorophenol to afford **3**. Complex **3** can be accessed directly in high yield *via* reaction of [$WCl_4(NNPh_2)$] and two equivalents of $NaOC_6F_5$ in thf. The molecular structure is shown in Fig. 3 with selected bond lengths and angles given in Table 3.

The structure has crystallographic C_2 symmetry about an axis passing along the tungsten–isodiazene linkage. The geometry at tungsten is distorted octahedral with *cis* angles in the range 80.9(1) to 99.1(1)° and a noticeably bent *trans* O–W–O angle of 161.8(3)°. There is a similar, but smaller, fold angle associated with the *trans* chlorides [Cl–W–Cl 170.84(9)°] which, coupled with the above distortion, results in the tungsten lying 0.26 Å out of the equatorial plane in the direction of the isodiazene ligand, and away from the co-ordinated thf. The equatorial W–O distance [1.934(5) Å] is as expected significantly shorter than that to the axial furan oxygen [2.215(6) Å] and also shorter than to the axial phenoxide in complex **2**. Interestingly, the W–N distance is unchanged [1.738(7) Å] from

Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

W–N(1)	1.738(7)	W–O(1)	1.934(5)
W–O(1′)	1.934(5)	W–O(2)	2.215(6)
W–Cl	2.360(2)	W–Cl′	2.360(2)
N(1)–N(2)	1.317(10)		
N(1)–W–O(1′)	99.1(1)	N(1)–W–O(1)	99.1(1)
O(1′)–W–O(1)	161.8(3)	N(1)–W–O(2)	180.0
O(1′)–W–O(2)	80.9(1)	O(1)–W–O(2)	80.9(1)
N(1)–W–Cl	94.58(4)	O(1′)–W–Cl	88.4(2)
O(1)–W–Cl	90.1(2)	O(2)–W–Cl	85.42(4)
N(1)–W–Cl′	94.58(4)	O(1′)–W–Cl′	90.1(2)
O(1)–W–Cl′	88.4(2)	O(2)–W–Cl′	85.42(4)
Cl–W–Cl′	170.84(9)	C(7)–O(1)–W	132.8(5)
N(2)–N(1)–W	180.0		

that observed in **2** where the co-ordination geometry is totally different and the σ donation of the pentafluorophenoxide group would be expected to be somewhat greater. The conformation is stabilised by pairs of intramolecular π–π stacking interactions between the isodiazene rings and their pentafluorophenoxy neighbours, the mean interplanar and centriod–centroid separations being 3.37 and 3.75 Å respectively. The pattern of stacking extends to include the pentafluorophenoxide ring of an adjacent C_i related molecule [mean interplanar and shortest internuclear F···C separations 3.36 and 3.36 Å respectively] resulting in the formation, *via* the C_2 symmetry, of zigzag chains of π–π linked molecules that extend in the crystallographic *c* direction.

Conclusion

The successful synthesis of $[Mo(CH_2CMe_2Ph)(NNPh_2)(OC_6F_5)]$ and $[W(CH_2SiMe_3)_3(NNPh_2)(OC_6F_5)]$ shows that alkylation of the mono-isodiazene $[M(NNPh_2)]$ core is much more favourable than for the related bis(isodiazene) $[M(NNPh_2)_2]$ core.[4] Upon warming in chlorobenzene solution, the air-stable five-co-ordinate trialkyl complex $[Mo(CH_2CMe_2Ph)_3(NNPh_2)(OC_6F_5)]$ gives an effective catalyst for metathesis polymerisation of norbornene in the absence of an activator. The tungsten complex $[W(CH_2SiMe_3)_3(NNPh_2)(OC_6F_5)]$ is somewhat less effective and gives broader molecular weight distribution poly(norbornene). These results represent the first indications that single-component isodiazene metathesis catalysts are accessible, though additional work will be required to improve the control features of the system.

Experimental

General

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Imperial College. The NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 (^1H), 75.0 (^{13}C) and 376.3 MHz (^{19}F) with chemical shifts referenced to the residual protio impurity of the deuteriated solvent, IR spectra (Nujol mulls, KBr windows) on Perkin-Elmer 577 and 457 grating spectrophotometers. The starting materials $[MoCl_4(NNPh_2)]$ and $[WCl_4(NNPh_2)]$ were prepared as described in the literature.[5] All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparations

Complex 1. To $[MoCl_4(NNPh_2)]$ (3.0 g, 7.8 mmol) in diethyl ether at −78 °C was added $PhCMe_2CH_2MgCl$ (11.7 cm³, 2.0 M solution in thf) *via* a syringe. Stirring was continued for 3 h at ambient temperature, the volatiles were removed *in vacuo* and the residue was taken up in pentane (2 × 30 cm³). After filtration, solid C_6F_5OH (2.87 g, 15.6 mmol) was added at −78 °C and stirring was continued for 2 h. Filtration, concentration (to *ca.* 30 cm³) and cooling to 0 °C afforded **1** as orange-red blocks. Yield 2.6 g, 41%. Found: C, 65.7; H, 5.2; N, 3.5. $C_{48}H_{49}F_5MoN_2O$ requires C, 66.0; H, 5.3; N, 3.4%. IR: 1649w, 1622w, 1588w, 1515s, 1504s, 1490s, 1324m, 1312m, 1275m, 1262s, 1207w, 1172s, 1157m, 1110m, 1090m, 1073m, 1024s, 980m, 921w, 893w, 850w, 801w, 758w, 749m, 738m, 723m, 702m, 692m, 660m and 647m cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 1.29 (s, 18 H, CMe_2), 2.63 (s, 6 H, CH_2) and 6.84–7.19 (overlapping multiplets, 15 H, aryl H). ^{13}C NMR (400 MHz, C_6D_6): δ 32.25 ($C\mathit{Me}_2$), 42.23 ($\mathit{C}Me_2$), 83.82 (CH_2), 118.13, 122.63, 125.50, 125.82, 126.00, 126.20, 129.21, 129.37, 129.50, 129.81, 140.53 and 151.16. ^{19}F NMR (400 MHz, C_6D_6): δ −162.48 (m, 2F, *o*-CF), −163.77 (m, 2F, *m*-CF) and −168.61 (m, 1F, *p*-CF).

Complex 2. As for complex **1**, but using $[WCl_4(NNPh_2)]$ (1.0 g, 1.97 mmol), Me_3SiCH_2MgCl (7.88 cm³, 1.0 M) and C_6F_5OH (0.73 g, 3.97 mmol) affording **2** as golden-yellow plates. Yield 0.48 g, 30%. Found: C, 43.9; H, 5.1; N, 3.5. $C_{30}H_{43}F_5N_2OSi_3W$ requires C, 44.4; H, 5.3; N, 3.5%. IR: 1649w, 1623w, 1592m, 1505s, 1494s, 1407m, 1342m, 1331m, 1316m, 1286m, 1247s, 1176s, 1075m, 1028s, 989s, 962s, 930m, 906m, 833s, 744s, 721m, 697s, 667s, 649m, 626m and 612m cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ −0.07 (s, 27 H, $SiMe_3$), 1.33 (s, 6 H, CH_2) and 7.17–7.48 (overlapping multiplets, 10 H, aryl H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 1.62 (s, $SiMe_3$), 66.41 (s, CH_2), 121.81, 125.49, 129.41 and 141.16 (only observed aryl C). ^{19}F NMR (400 MHz, $CDCl_3$): δ −157.37 (m, 2F, *o*-CF), −165.25 (m, 2F, *m*-CF) and −172.40 (m, 1F, *p*-CF).

Complex 3. As for complex **1**, but using $[WCl_4(NNPh_2)]$ (1.0 g, 1.97 mmol), $PhCH_2MgCl$ (7.88 cm³, 1.0 M solution) and C_6F_5OH (0.73 g, 3.97 mmol) affording **3** as golden-yellow plates. Yield 0.41 g, 24.3%. Found: C, 40.4; H, 2.4; N, 2.8. $C_{28}H_{18}Cl_2F_{10}N_2O_3W$ requires C, 39.1; H, 2.1; N, 3.3%. IR: 1590w, 1510s, 1308m, 1264w, 1192w, 1155m, 1063w, 1018s, 1000s, 987s, 917w, 881w, 844w, 753m, 721m, 692m and 676m cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.19 (m, 4 H, thf), 4.69 (m, 4 H, thf) and 7.03–7.52 (overlapping multiplets, 10 H, aryl H). ^{19}F NMR (400 MHz, $CDCl_3$): δ −157.84 (m, 4F, *o*-CF), −163.55 (m, 4F, *m*-CF) and −165.45 (m, 2F, *p*-CF).

X-Ray crystallography

Table 4 provides a summary of the crystal data, data collection and refinement parameters for complexes **1**, **2** and **3**. The structures of **1** and **2** were solved by direct methods, that of **3** by the heavy atom method, and the refinements were by full matrix least squares based on F^2. The pendant phenyl rings were refined as idealised rigid bodies and all of the non-hydrogen atoms were refined anisotropically. The C–H hydrogen atoms in all three structures were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$ [$U(H) = 1.5U_{eq}(C\text{–}Me)$], and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system.[7]

CCDC reference number 186/1540.

See http://www.rsc.org/suppdata/dt/1999/2701/ for crystallographic files in .cif format.

Acknowledgements

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Table 4 Crystal data, data collection and refinement parameters[a] for complexes **1**–**3**

	1	**2**	**3**
Formula	$C_{48}H_{49}F_5MoN_2O$	$C_{30}H_{43}F_5N_2OSi_3W$	$C_{28}H_{18}Cl_2F_{10}N_2O_3W$
Formula weight	860.8	810.8	875.2
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P1$ (no. 2)	$P1$ (no. 2)	$C2/c$ (no. 15)
T/K	203	293	293
a/Å	11.809(3)	9.997(1)	10.908(2)
b/Å	11.905(1)	10.664(1)	13.007(2)
c/Å	16.348(3)	18.101(1)	21.660(4)
α/°	87.30(1)	90.84(1)	—
β/°	81.01(2)	90.34(1)	98.29(2)
γ/°	66.88(1)	110.94(1)	—
V/Å^3	2087.5(7)	1802.0(3)	3041.0(9)
Z	2	2	4[b]
D_c/g cm^{-3}	1.370	1.494	1.912
Radiation used	Cu-Kα[c]	Cu-Kα	Mo-Kα
μ/mm^{-1}	3.07	7.33	4.07
No. unique reflections			
measured	6537	5327	2412
observed, $\lvert F_o \rvert > 4\sigma(\lvert F_o \rvert)$	6227	4795	2050
$R1$	0.041	0.046	0.036
$wR2$	0.110	0.117	0.080

[a] Details in common: graphite monochromated radiation, ω scans, Siemens P4 diffractometer. [b] The complex has crystallographic C_2 symmetry. [c] Rotating anode source.

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