Journal of Organometallic Chemistry, 260 (1984) 99–104
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS AND CRYSTAL STRUCTURE OF t-BUTYLISOCYANIDENONACARBONYLDIRHENIUM(0): $Re_2(CO)_9(CNBu^t)$

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(Received August 12th, 1983)

Summary

The compound $Re_2(CO)_9(CNBu^t)$ was synthesized in high yield by the PdO catalysed reaction between $Re_2(CO)_{10}$ and Bu^tNC. The molecular structure of this complex has been determined by X-ray crystallography: Space group: *Pbca*, *a* 17.160(7), *b* 18.300(7), *c* 12.370(5) Å, *V* 3884.53 Å^3, $Z = 8$, $R = 0.0994$. The structure of the dimer has a staggered configuration with the isonitrile ligand occupying an equatorial position.

Transition metal complexes containing metal–metal bonds (metal clusters), comprise an important class of inorganic compounds [1,2]. The simplest members of the metal cluster complexes are the metal dimers and these dimers provide a starting point for an understanding of the chemistry and reactivity of the higher members of the cluster complexes. Herein we wish to report our preliminary results on an extension of our catalytic route [3] to the substitution of the metal dimer, $Re_2(CO)_{10}$, and the stereochemistry of the products formed by successive displacement of CO ligands on $Re_2(CO)_{10}$ by donor ligands (e.g. isonitriles, phosphines etc). In particular, this publication contains our results on the crystal structure determination (and synthesis) of $Re_2(CO)_9(CNBu^t)$. There is only one other mention of the reaction between $Re_2(CO)_{10}$ and isonitrile in the literature and in this publication only the IR spectrum of $Re_2(CO)_9(CNCH_3)$ was reported [4].

Experimental

$Re_2(CO)_{10}$ was purchased from Strem Chemicals, Bu^tNC from Fluka AG and PdO from Johnson–Matthey Pty. Ltd. The IR spectrum was recorded on a Pye Unicam SP300 spectrophotometer, the ^1H NMR spectrum on a Bruker WP80 FTNMR spectrometer and the mass spectrum on a Varian MAT CH5 spectrometer.

Reactions were carried out under nitrogen and column chromatography was performed on silica gel (Merck 'Kieselgel 60', 60–200 μm).

0022-328X/84/$03.00

Synthesis of $Re_2(CO)_9(CNBu^t)$

$Re_2(CO)_{10}$ (1.0 mmol) and PdO (20 mg) were stirred in toluene (10 ml) at 55°C. Bu^tNC (1.0 mmol) was then added to the solution via a syringe. Within 1 minute conversion of $Re_2(CO)_{10}$ to $Re_2(CO)_9(NCBu^t)$ was complete as evidenced by thin layer chromatography (silica gel, hexane/benzene (20%) as eluent).

The product was isolated by column chromatography (silica gel, hexane/benzene (20%) as eluent), and recrystallized from dichloromethane/hexane to yield white needles (90%), m.p. 104–106°C, ν(NC): 2173, ν(CO): 2101, 2050, 2018, 1996, 1979(w), 1970, 1952 cm^{-1} (hexane); δ (C_6D_6): 0.75 (s, Me) ppm; mol. mass: 708 (mass spectrometry). Found C, 24.16; H, 1.24; N, 1.84. $Re_2C_{14}H_9NO_9$ calcd.: C, 23.77; H, 1.28; N, 1.98%.

Crystallographic analysis

White needle-like crystals of $Re_2(CO)_9(CNBu^t)$ were obtained from CH_2Cl_2 hexane solution at 20°C. Crystal data and experimental details of the crystallographic analysis are summarised in Table 1. The data were corrected for Lorentz-polarization effects, but not for absorption. Crystallographic computations were performed using the program SHELX [5]. The positions of the two rhenium atoms in the asymmetric unit were derived from a Patterson synthesis, and the other non-hydrogen atoms placed by difference Fourier syntheses.

The positional parameters of all atoms, and the anisotropic temperature factors for the rhenium atoms, were refined by full matrix least-squares analyses, until all parameter shifts were less than 0.5σ, by which stage $R = 0.0994$. Unit weights were

TABLE 1

CRYSTAL DATA AND DETAILS OF THE X-RAY INTENSITY MEASUREMENTS

Molecular formula	$Re_2C_{14}H_9NO_9$
M.w.	707.62
Space group	*Pbca*
a	17.160(7) Å
b	18.300(7) Å
c	12.370(5) Å
U	3884.53 $Å^3$
Z	8
D_c	2.42 g cm^{-3}
F(000)	2575
μ(Mo-K_α)	119.17 cm^{-1}
Crystal dimension	0.19×0.18×0.13 mm
Diffractometer	Philips PW1100 four circle
Radiation	Mo-K_α (λ 0.7107 Å)
Scan mode	$\omega-2\theta$
Range	$3 \geq \theta \geq 25°$
Scan width	1.20°
Scan speed	0.040° s^{-1}
Background count	30 s
Measured intensities	2522
Unique reflections	2168
Cut off criteria	$F < \sigma F$
Observed intensities	2043
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.0994

TABLE 2(a)

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC THERMAL VIBRATION PARAMETERS (Å^2) FOR THE NON-METAL ATOMS

Atom	x/a	y/b	z/c	U
Re(1)	0.3693(1)	−0.1472(1)	−0.2994(1)	–
Re(2)	0.2235(1)	−0.0982(1)	−0.1789(1)	–
O(1)	0.285(2)	−0.294(2)	−0.333(3)	0.084(9)
O(2)	0.520(2)	−0.203(2)	−0.409(3)	0.071(8)
O(3)	0.289(2)	−0.087(2)	−0.516(3)	0.093(10)
O(4)	0.425(2)	−0.203(2)	−0.069(4)	0.111(12)
O(5)	0.223(2)	−0.248(2)	−0.069(3)	0.085(9)
O(6)	0.124(2)	−0.169(2)	−0.367(3)	0.113(12)
O(7)	0.083(2)	−0.040(2)	−0.054(3)	0.093(10)
O(8)	0.247(2)	0.045(2)	−0.311(2)	0.071(8)
O(9)	0.346(2)	−0.037(2)	−0.015(3)	0.089(10)
N	0.434(2)	0.012(1)	−0.260(3)	0.044(7)
C(1)	0.320(2)	−0.240(2)	−0.316(3)	0.040(8)
C(2)	0.463(2)	−0.181(2)	−0.368(3)	0.047(9)
C(3)	0.321(3)	−0.105(3)	−0.455(5)	0.083(14)
C(4)	0.408(3)	−0.186(3)	−0.152(5)	0.079(14)
C(5)	0.220(3)	−0.193(2)	−0.111(4)	0.069(12)
C(6)	0.160(3)	−0.148(3)	−0.297(4)	0.085(14)
C(7)	0.133(3)	−0.061(2)	−0.102(4)	0.069(12)
C(8)	0.235(2)	−0.008(2)	−0.256(3)	0.044(9)
C(9)	0.299(3)	−0.049(3)	−0.075(4)	0.081(14)
C(10)	0.414(2)	−0.044(1)	−0.277(3)	0.023(7)
C(11)	0.460(2)	0.087(2)	−0.234(4)	0.057(11)
C(12)	0.536(8)	0.070(7)	−0.155(11)	0.320(65)
C(13)	0.437(6)	0.143(6)	−0.298(9)	0.216(42)
C(14)	0.396(8)	0.116(7)	−0.110(11)	0.288(62)

TABLE 2(b)

ANISOTROPIC THERMAL VIBRATION PARAMETERS ($U_{ij}\times10^4$ Å^2) OF THE RHENIUM ATOMS

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re(1)	430(8)	381(8)	407(13)	−5(7)	−42(7)	3(6)
Re(2)	419(8)	540(9)	441(14)	24(8)	−4(7)	−25(7)

used, scattering factors for Re^0 were taken from International Tables Vol IV [6], and anomalous dispersion corrections for rhenium were made [7]. The refined atomic coordinates and thermal vibration parameters are given in Table 2.

Results and discussion

The 1/1 reaction between Re$_2$(CO)$_{10}$ and Bu^{t}NC with PdO as catalyst provides a facile synthetic route to Re$_2$(CO)$_9$(CNBu^t) in high yield. The corresponding reaction in the absence of catalyst is slow (210 min versus 1 min for the catalysed reaction at 55°C). The product was characterized by IR, NMR, mass spectrometry and elemental analyses (see Experimental). Although the above results unambiguously establish that only monosubstitution of $Re_2(CO)_{10}$ by Bu^tNC has occurred, the data do not unambiguously establish the stereochemistry of the reaction product [8,9]. It was thus decided to ascertain the stereochemistry of $Re_2(CO)_9(CNBu^t)$ by means of a crystal structure determination.

Crystal structure determination

The molecular structure of $Re_2(CO)_9(CNBu^t)$ and the numbering system used in the crystal structure determination is shown in Fig. 2. Selected bond lengths and bond angles are given in Tables 3 and 4 respectively. Two features of the crystal structure are immediately apparent: (a) the isonitrile occupies an equatorial position (Fig. 1a) and (b) the two halves of the molecule are staggered with respect to each other.

The axial Re–CO bond distance (avg. value, 1.93(4) Å) is shorter than the average equatorial Re–CO bond distance (avg. value 2.04(5) Å, excluding Re–C(1) in which the CO group is *trans* to the Bu^tNC group (1.91(3) Å). This effect of a shorter Re–CO (axial) bond distance relative to the Re–CO equatorial bond distance, has been observed in the structure of $Re_2(CO)_{10}$ [10], and can be ascribed to competition for $d\pi$ electron density between mutually *trans* pairs of equatorial carbonyls. The shorter Re–C(1) bond distance could also reflect the greater π-acceptor ability of the CO group relative to the Bu^tNC group [11]. The Re–Re bond length (3.048(2) Å) is not significantly longer than that of the value measured in $Re_2(CO)_{10}$ (3.0413(11) Å) [10].

The Re–Re–C (equatorial) angles range from 85(1) to 91(1)° averaging 87° i.e. the CO ligands bend in towards the metal–metal bond. The OC(axial)–M–CO

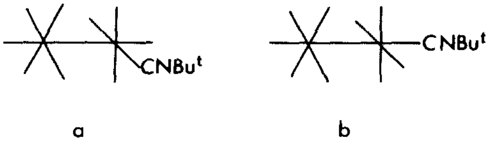

Fig. 1. Two possible structures of $Re_2(CO)_9(CN^tBu)$ (a) equatorial substitution, (b) axial substitution.

TABLE 3

BOND LENGTHS (Å)

Re(1)–Re(2)	3.048(2)
Re(1)–C(1)	1.91(3)
Re(1)–C(2)	1.92(4)
Re(1)–C(3)	2.23(6)
Re(1)–C(4)	2.07(6)
Re(2)–C(5)	1.93(4)
Re(2)–C(6)	2.04(5)
Re(2)–C(7)	1.94(5)
Re(2)–C(8)	1.92(4)
Re(2)–C(9)	2.04(5)
Re(1)–C(10)	2.05(3)
C(10)–N	1.10(4)
C(11)–N	1.47(4)

TABLE 4

BOND ANGLES (°)

Re(1)-C(1)-O(1)	174(3)	Re(2)-C(5)-O(5)	176(4)
Re(1)-C(2)-O(2)	179(3)	Re(2)-C(6)-O(6)	173(5)
Re(1)-C(3)-O(3)	169(5)	Re(2)-C(7)-O(7)	177(4)
Re(1)-C(4)-O(4)	175(5)	Re(2)-C(8)-O(8)	173(3)
Re(1)-C(10)-N	176(3)	Re(2)-C(9)-O(9)	165(4)
C(1)-Re(1)-Re(2)	87(1)	C(5)-Re(2)-Re(1)	89(1)
C(2)-Re(1)-Re(2)	177(1)	C(6)-Re(2)-Re(1)	88(1)
C(3)-Re(1)-Re(2)	91(1)	C(7)-Re(2)-Re(1)	177(1)
C(4)-Re(1)-Re(2)	86(1)	C(8)-Re(2)-Re(1)	86(1)
C(10)-Re(1)-Re(2)	88(1)	C(9)-Re(2)-Re(1)	85(1)
C(10)-N-C(11)	178(4)		

(equatorial) angles, as expected, are all > 90°C. Similar trends were observed in $Re_2(CO)_{10}$ [10] and have been rationalised by Elian and Hoffmann [12]. Also significant is the observation that the Re–Re–C (isonitrile) angle is less than 90° (88(1)°). Since Bu^tNC has a larger cone angle [13] than CO, the results indicate that any steric factors are less important than electronic factors in determining the direction of the bending of the equatorial ligands.

The equatorial substitution of CO by $CNBu^t$ is in keeping with previous arguments on the final position of the incoming ligand in an octahedral environment [14]. Deviations from this rule have been observed [14] and have been ascribed to steric factors. Although no crystal structure data are presently available on complexes of the type $Re_2(CO)_9L$ or $Re_2(CO)_8L_2$ (L = bulky ligand) it might be anticipated that these will contain axial substituents [15] consistent with studies on the analogous Mn derivatives [16].

As shown in Fig. 2 the two halves of the dimer are staggered with the Bu^tNC ligand aligning itself between the 2 CO ligands on the opposite Re atom. This staggered geometry presumably arises from steric considerations (i.e. reduced interaction of equatorial CO groups on the two Mn atoms) and has been observed in most $M_2(CO)_{10-x}(L)_x$ (M = Mn, Re; $x = 0$–2, L = donor ligand) complexes [10,15].

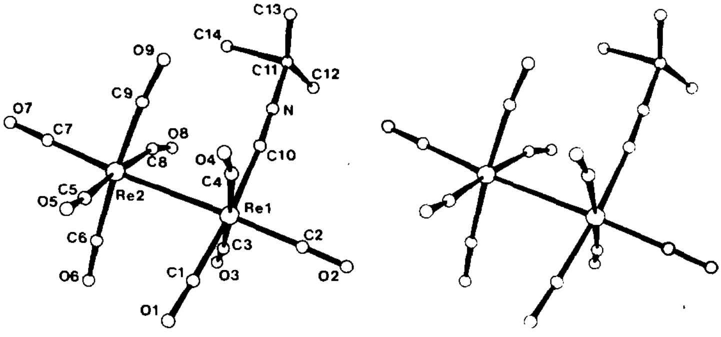

Fig. 2. ORTEP [17] view of the molecule.

Conclusion

The crystal structure determination unambiguously reveals that equatorial substitution of $Re_2(CO)_{10}$ by Bu^tNC has occurred. The scope of the catalytic synthetic procedure is being further investigated in the preparation of higher substituted derivatives $Re_2(CO)_{10-x}(CNR)_x (x > 1)$ in the anticipation that structural studies will provide a rationalization for the reactivity and stereochemistry of the metal dimers.

Acknowledgements

We wish to thank the CSIR and the University for financial assistance. We would also like to thank Mr. J. Albain for collecting the X-ray crystallographic data.

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