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Synthesis and molecular structure of octacarbonyl[bis(diphenylarsenido)]dirhenium, $Re_2(CO)_8[\mu\text{-}As(C_6H_5)_2]_2$, resulting from the $Re_2(CO)_{10}$ catalyzed disproportionation of phenylarsinidine

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Abstract

The X-ray crystallographic structure determination of $Re_2(CO)_8[\mu\text{-}As(C_6H_5)_2]_2$ shows that the compound crystallizes in the monoclinic space group $P2_1/n$ with a 12.284(4), b 16.897(6), c 15.880(8) Å, β 100.31(3)°, V 3243(2) Å^3 and $Z = 4$. Least squares refinement based on 3807 independent observed data resulted in a final $R(F)$ value of 4.46%. The Re_2As_2 core is slightly bent with $Re(CO)_4$ groups staggered an average of 12.6°; the Re ··· Re separation of 4.090(1) Å precludes metal–metal bonding. The formation of $Re_2(CO)_8[\mu\text{-}As(C_6H_5)_2]_2$ results from the disproportionation of phenylarsinidine and is accompanied by the formation of naked arsenic-atom clusters.

Introduction

One of the most conspicuous features of catenated organoarsines as they enter into reactions with metal carbonyls is the ease and unpredictability with which they lose organic groups in their adaptation to the steric and electronic demands of the metallic groups. Very recent examples are found in the reactions of $Co_2(CO)_8$ [1] or $Re_2(CO)_{10}$ [2] with pentamethylcyclopentaarsine and hexaphenylcyclohexaarsine. Under conditions (< 70 °C) mild enough that the cycloarsines are themselves indefinitely stable, methyl and phenyl substitution is lost to accommodate formation of 18-electron metal environments.

A question which we previously have not been able to answer authoritatively concerns the fate of the dissociated organic group. One pattern that emerges from many recent studies with metal carbonyls from groups 5 to 9 is the frequency with which dinuclear bis(μ-diorganoarsinido) complexes, $[L_nM(\mu\text{-}R_2As)]_2$, are found in varying quantities as coproducts in reactions yielding clusters with naked arsenic atoms. This suggests that the formation of naked arsenic results by a disproportionation reaction which may be schematically represented as

$$2RAs \rightarrow R_2As + As$$

In support of this, neat *cyclo*-$(MeAs)_5$ at high temperatures slowly forms tetramethyldiarsine and deposits arsenic mirrors [3]. Thus, the metal carbonyl appears to promote this process catalytically.

From the further workup of the reaction products obtained in our study of cyclopolyarsine reactions with $Re_2(CO)_{10}$ which form naked arsenic atom products [2], we have isolated the colorless and previously overlooked product $[Re(CO)_4(\mu\text{-}Ph_2As)]_2$ (I), whose crystal structure we now report. Although $[Mn(CO)_4(\mu\text{-}R_2P)]_2$ (R = Me or Ph) products have been reported [4], and the methyl derivative structurally characterized, no complexes of this type containing Re and none for any group 7 metal containing arsenido groups have been reported previously.

Experimental

Preparation of $Re_2(CO)_8[As(C_6H_5)_2]_2$ *(I)*

Unless otherwise specified, all manipulations were carried out under an atmosphere of N_2 or in evacuated (Carius) tubes. Melting points were measured on a Mel-Temp apparatus and were uncorrected. Infrared spectra were recorded on a Nicolet 50XB FTIR spectrophotometer as KBr pellets or as solutions in CH_2Cl_2. ^1H NMR spectra were obtained on a Bruker 250 MHz spectrometer with TMS as an internal reference.

Toluene, methylene chloride and pentane were all purified and distilled under N_2 according to established procedures. $Re_2(CO)_{10}$ (Strem) was sublimed before use. $(C_6H_5As)_6$ was prepared by a published procedure [5].

Caution: The following reaction involves the use of sealed, medium-walled glass Carius tubes. These tubes, when heated, may reach pressures of up to 30 atm and occasionally explode. All heating of these tubes should be done only after placing the sealed tube in an end-capped, perforated steel tube.

In a medium-walled Carius tube 1.053 g (1.61 mmol) of $Re_2(CO)_{10}$ and 3.00 (3.28 mmol) of $(C_6H_5As)_6$ were combined with 15 ml of toluene. The tube was evacuated with three freeze-pump-thaw cycles, flame sealed, and placed in an oven at 130 °C for 72 h. The initially pale yellow solution became orange-red. The Carius tube was cooled to $-15\,^\circ C$ for several days before opening.

Filtration of the chilled tube yields a colorless crystalline material identified as $[As(C_6H_5)_2]_2$. The orange-yellow filtrate was evaporated to dryness, and the residue redissolved in a minimum of toluene and eluted on an alumina column with 10% toluene in hexanes. In addition to the previously described [2] Re–As cluster species, $[Re_3(CO)_{10}(C_6H_5As)_7As]$, a colorless band from the column yielded $Re_2(CO)_8[\mu\text{-}As(C_6H_5)_2]_2$ (I) which was isolated as colorless crystals grown from CH_2Cl_2/pentane (yield 8%). Decomposition 281–285 °C. IR (CH_2Cl_2): $\nu(CO)$, 2091 (s), 2073 (s), 2006 (s), 1994 (s), 1982 (s), 1974 (s), 1955 (s), 1935 (s) cm^{-1}. ^1H NMR ($CDCl_3$): aromatic complex δ 7.23–7.56 ppm. Anal. Found: C, 36.66; H, 1.79; As, 14.00. $C_{32}H_{20}As_2O_8Re_2$ calcd.: C, 36.42; H, 1.91; As, 14.21%.

Table 1

Crystal and data parameters at 293 K

Compound	$Re_2(CO)_8[\mu\text{-}As(C_6H_5)_2]_2$
Formula	$C_{32}H_{20}O_8As_2Re_2$
Space group	monoclinic, $P2_1/n$
a, Å	12.284(4)
b, Å	16.897(6)
c, Å	15.880(8)
β, deg	100.31(3)
V, Å^3	3243(2)
Z	4
ρ(calcd), g cm^{-3}	2.16
Crystal dimension, mm	$0.35 \times 0.35 \times 0.35$
μ, cm^{-1}	100.8
Radiation	graphite-monochromated Mo-K_α
Diffractometer	Nicolet R3m/μ
T(max)/T(min)	0.165/0.118
Scan speed, deg min^{-1}	variable, 5–20
2θ scan limits, deg	$4 \leq 2\theta \leq 52$
Scan method	Wyckoff
Data collected	$\pm h, +h, +l$
Standard reflections	3 std/97 rflns (var. $<1\%$)
Unique data	6379 (6613 collected)
Unique data, $F_o \geq 5\sigma(F_o)$	3807
R(int), %	3.45
Number of parameters	349
$R(F)$, $R(wF)$, %	4.46, 4.51
GOF	1.115
$\Delta(\rho)$ max, e Å^{-3}	1.37 (0.89 Å from Re(1))
Δ/σ max	0.018
g, $w^{-1} = \sigma^2(F_o) + g(F_o)^2$	0.001

X-ray structure determination

A colorless crystal of $C_{32}H_{20}As_2O_8Re_2$ (I) was attached to a fine glass fiber with epoxy cement. The monoclinic space group $P2_1/n$ was unambiguously assigned from the systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$). Lattice parameters were derived from the least squares fit of 25 reflections with $21° \leq 2\theta \leq 28°$. The parameters used during the collection of diffraction data are contained in Table 1. Intensity data were empirically corrected for absorption.

The structure of I was solved via direct methods (SOLV) which located the Re and As atoms. The remaining nonhydrogen atoms were located from subsequent difference Fourier syntheses. Nonhydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and fixed in idealized positions (d(C–H) 0.96 Å, $U = 1.2$ times U_{iso} for the carbon to which it was attached). Phenyl rings were constrained to fit rigid hexagons (d(C–C) 1.395 Å). Computer programs used in the collection and refinement of data are contained in the Nicolet (Madison, WI) program packages, P3, SHELXTL (version 5.1).

Atomic coordinates are given in Table 2, and bond distances and angles in Table 3. Tables of anisotropic temperature factors, hydrogen atom coordinates, and structure factors may be obtained from the authors.

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$)

	x	y	z	U [a]
Re(1)	2600.9(4)	3320.6(3)	2782.8(3)	35.5(2)
Re(2)	4680.2(4)	1706.9(3)	4157.2(3)	37.7(2)
As(1)	2923.2(9)	2549.8(7)	4230.1(8)	33.6(4)
As(2)	4427.8(9)	2547.9(7)	2765.7(7)	32.4(4)
C(1)	2466(11)	3717(8)	1630(9)	57(5)
O(1)	2437(9)	3971(7)	960(6)	82(5)
C(2)	1702(11)	2376(8)	2389(8)	53(5)
O(2)	1149(9)	1840(7)	2185(7)	88(5)
C(3)	1274(12)	3878(8)	2993(10)	55(5)
O(3)	501(9)	4164(7)	3118(8)	90(5)
C(4)	3524(12)	4227(8)	3227(9)	56(5)
O(4)	4071(10)	4773(7)	3430(8)	95(6)
C(5)	6032(13)	1205(9)	3995(9)	63(6)
O(5)	6822(9)	903(8)	3871(8)	91(5)
C(6)	3821(11)	927(7)	3406(9)	51(5)
O(6)	3352(9)	455(6)	2939(8)	78(5)
C(7)	4623(12)	1105(8)	5201(10)	59(6)
O(7)	4568(10)	735(7)	5797(8)	94(5)
C(8)	5453(11)	2579(9)	4849(9)	57(5)
O(8)	5869(9)	3099(8)	5207(7)	93(5)
C(11)	3161(7)	4007(5)	5280(5)	55(5)
C(12)	3365	4421	6053	78(7)
C(13)	3485	4011	6827	77(7)
C(14)	3400	3188	6828	62(6)
C(15)	3196	2774	6056	56(5)
C(16)	3076	3184	5282	48(5)
C(21)	1572(6)	1118(4)	4280(6)	55(5)
C(22)	581	718	4289	68(6)
C(23)	−363	1138	4393	70(7)
C(24)	−316	1959	4489	64(6)
C(25)	675	2359	4480	56(5)
C(26)	1619	1939	4376	40(4)
C(31)	5623(6)	3658(5)	1894(5)	53(5)
C(32)	6526	4103	1744	71(6)
C(33)	7521	4079	2326	59(6)
C(34)	7613	3610	3059	60(6)
C(35)	6710	3165	3209	50(5)
C(36)	5715	3189	2627	37(4)
C(41)	5364(5)	1479(5)	1662(5)	48(5)
C(42)	5354	965	973	73(7)
C(43)	4381	853	381	74(7)
C(44)	3419	1255	477	77(7)
C(45)	3430	1769	1166	66(6)
C(46)	4402	1881	1759	35(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Discussion

The structure and labelling scheme of I are shown in Fig. 1. Figure 2 shows a stereoview of the unit-cell packing. The structural features of $[L_nM(\mu\text{-}R_2E)]_2$ complexes have been reviewed [6].

Table 3

Bond lengths (Å) and bond angles (°)

Re(1)-As(1)	2.609(1)	As(1)-C(16)	1.965(8)
Re(1)-As(2)	2.601(1)	As(1)-C(26)	1.954(8)
Re(1)-C(1)	1.928(15)	As(2)-C(36)	1.962(8)
Re(1)-C(2)	1.977(13)	As(2)-C(46)	1.952(8)
Re(1)-C(3)	1.962(15)	C(1)-O(1)	1.142(18)
Re(1)-C(4)	1.961(14)	C(2)-O(2)	1.144(17)
Re(2)-As(1)	2.606(1)	C93)-O(3)	1.115(19)
Re(2)-As(2)	2.599(1)	C(4)-O(4)	1.152(18)
Re(2)-C(5)	1.922(16)	C(5)-O(5)	1.144(20)
Re(2)-C(6)	1.955(13)	C(6)-O(6)	1.168(17)
Re(2)-C(7)	1.958(16)	C(7)-O(7)	1.146(20)
Re(2)-C(8)	1.977(14)	C(8)-O(8)	1.119(19)
As(1)-Re(1)-As(2)	76.3(1)	C(7)-Re(2)-C(8)	90.2(6)
As(1)-Re(1)-C(1)	169.5(4)	Re(1)-As(1)-Re(2)	103.3(1)
As(2)-Re(1)-C(1)	95.3(4)	Re(1)-As(1)-C(16)	116.9(2)
As(1)-Re(1)-C(2)	82.2(4)	Re(2)-As(1)-C(16)	112.4(3)
As(2)-Re(1)-C(2)	91.5(4)	Re(1)-As(1)-C(26)	111.7(3)
C(1)-Re(1)-C(2)	91.8(6)	Re(2)-As(1)-C(26)	114.8(2)
As(1)-Re(1)-C(3)	95.2(4)	C(16)-As(1)-C(26)	98.2(4)
As(2)-Re(1)-C(3)	170.9(4)	Fe(1)-As(2)-Re(2)	103.7(1)
C(1)-Re(1)-C(3)	93.5(6)	Re(1)-As(2)-C(36)	116.0(2)
C(2)-Re(1)-C(3)	90.4(6)	Re(2)-As(2)-C(36)	115.0(2)
As(1)-Re(1)-C(4)	94.9(4)	Re(1)-As(2)-C(46)	114.3(2)
As(2)-Re(1)-C(4)	87.2(4)	Re(2)-As(2)-C(46)	111.3(3)
C(1)-Re(1)-C(4)	90.9(6)	C(36)-As(2)-C(46)	97.0(3)
C(2)-Re(1)-C(4)	177.0(5)	Re(1)-C(1)-O(1)	176.5(13)
C(3)-Re(1)-C(4)	90.5(6)	Re(1)-C(2)-O(2)	176.9(13)
As(1)-Re(2)-As(2)	76.4(1)	Re(1)-C(3)-O(3)	177.0(13)
As(1)-Re(2)-C(5)	171.6(5)	Re(1)-C(4)-O(4)	175.2(14)
As(2)-Re(2)-C(5)	95.9(4)	Re(2)-C(5)-O(5)	177.8(12)
As(1)-Re(2)-C(6)	92.0(4)	Re(2)-C(6)-O(6)	176.7(13)
AS(2)-Re(2)-C(6)	83.1(4)	Re(2)-C(7)-O(7)	177.8(11)
C(5)-Re(2)-C(6)	90.3(6)	Re(2)-C(8)-O(8)	176.3(12)
As(1)-Re(2)-C(7)	95.2(4)	As(1)-C(16)-C(11)	122.6(2)
As(2)-Re(2)-C(7)	171.0(4)	As(1)-C(16)-C(15)	117.2(2)
C(5)-Re(2)-C(7)	92.7(6)	As(1)-C(26)-C(21)	122.1(2)
C(6)-Re(2)-C(7)	94.0(6)	As(1)-C(26)-C(25)	117.5(2)
As(1)-Re(2)-C(8)	83.5(4)	As(2)-C(36)-C(31)	117.4(2)
As(2)-Re(2)-C(8)	92.2(4)	As(2)-C(36)-C(35)	122.5(2)
C(5)-Re(2)-C(8)	93.6(6)	As(2)-C(46)-C(41)	118.8(2)
C(6)-Re(2)-C(8)	174.1(6)	As(2)-C(46)-C(45)	121.1(2)

The monoclinic unit cell contains four well separated molecules of I which have no crystallographically imposed symmetry. The structure consists of two $Re(CO)_4$ units bridged by two $As(C_6H_5)_2$ units. There is no Re-Re bond; the Re ··· Re distance is 4.090(1) Å.

The structure of I is very similar to the group 7 complex $(CO)_4Mn(\mu\text{-}PMe_2)_2Mn(CO)_4$ (II) [4] and one of two forms of the group 9 complex $(CO)_3Co(\mu\text{-}PPh_2)_2Co(CO)_3$ (III) [7]. All three have metal-metal bond orders of zero to maintain saturated 18-electron counts. II has crystallographically imposed $\bar{1}$ symmetry; III has 2 distinct structural forms in its asymmetric unit. In each of the three

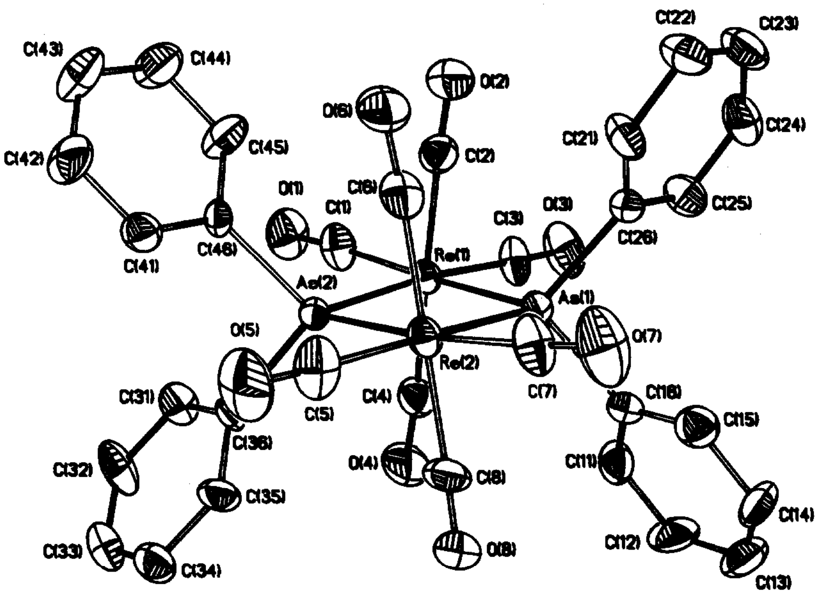

Fig. 1. Molecular structure and labeling scheme for $Re_2(CO)_8[\mu\text{-}As(C_6H_5)_2]_2$ (I) with 50% thermal ellipsoids. Hydrogen atoms are deleted for clarity.

isoelectronic complexes, the average M–E–M and E–M–E bond angles are similar: (av) As–Re–As, 76.4°, P–Mn–P, 76.9°, (av) P–Co–P, 74.5°; (av) Re–As–Re, 103.5°, Mn–P–Mn, 103.1°, (av) Co–P–Co, 103.8°.

The Re_2As_2 core in I is slightly bent, with the dihedral angle of 4.5° between the two As–Re–As planes. II, on the other hand, is rigorously planar, as required by the $\bar{1}$ symmetry. III has two distinct forms, A and B (molecule A is bent 2.6°, B is bent 25.0°). The co-crystallization of these two forms in III suggests there is little energy difference between bent and planar forms of these complexes. Complex I, however, with four CO ligands about each metal may energetically favor a nearly planar

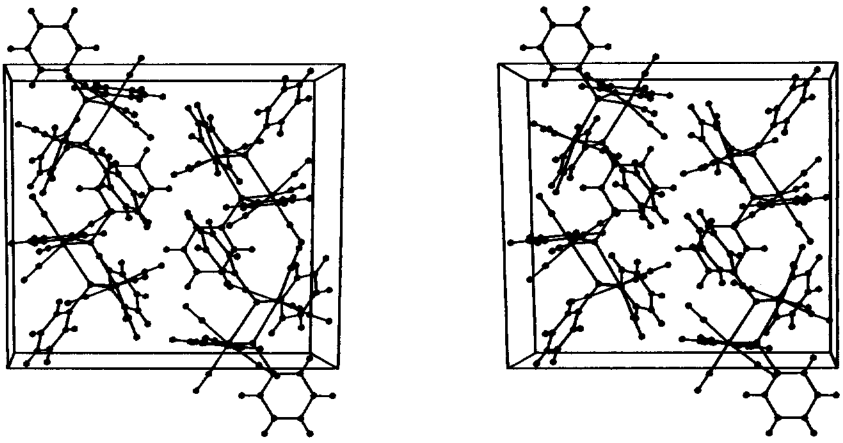

Fig. 2. A stereoview of the unit cell packing for I viewed along the a axis.

structure to minimize crowding. Evidence for close steric interactions is seen in short intramolecular contacts: C(2) $\cdots$ H(45), 2.50 Å, and C(6) $\cdots$ H(21), 2.53 Å. Both contacts are well within the sums of their Van der Waals radii (~ 2.9 Å) [8].

This steric crowding may be further relieved through the staggering of CO groups on the metal atoms. Looking down the metal–metal bond, CO groups on the Mn complex II are perfectly eclipsed as required by the $\bar{1}$ symmetry. III has two forms: The CO's of planar form B are almost perfectly staggered; bent form A has nearly eclipsed CO atoms. The title compound I is intermediate between the two forms of III; CO groups are staggered an average of 12.6° (range 9.0 to 14.7°). This staggering of the CO groups in combination with the short intramolecular contacts support the presence of strong steric interaction between the $Re(CO)_4$ and $As(C_6H_5)_2$ groups. Similar effects are also seen in metal–metal bonded complexes, in particular, $Mo_2(CO)_8[\mu\text{-}As(C_6F_5)_2]_2$ [9].

Conclusions

The frequent isolation of binuclear, bis-diorganoarsenido containing complexes as coproducts in reactions featuring the formation of naked arsenic containing clusters and the absence of other secondary or tertiary arsenic species, leads us to conclude that the $2RAs \rightarrow R_2As + As$ disproportionation is the primary, if not sole, fate of the lost organic substitution. The R_2As radicals may either first dimerize or react directly with available metallic species to form the arsenido complexes.

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