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Synthesis and Characterization of New Formamido-Complexes of Rhenium(I). The Crystal Structure of $[Re(CO)_2(p\text{-}NO_2C_6H_4N\overset{..}{-}CH\overset{..}{-}O)(PPh_3)_2]$

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The compound $[Re(CO)_3(PPh_3)_2Cl]$ *reacts with* $Li(O\overset{..}{-}CH\overset{..}{-}NAr)$ *(Ar =* C_6H_5, p-$CH_3C_6H_4$, p-ClC_6H_4, p-$CH_3OC_6H_4$, p-$NO_2C_6H_4$, o-$CH_3C_6H_4$*) in boiling tetrahydrofuran or toluene to yield new complexes of* Re^I *of the type* $[Re(CO)_2(ArN\overset{..}{-}CH\overset{..}{-}O)(PPh_3)_2]$. *The IR spectra suggest that the ligand is chelated and that the two CO groups are in* cis *positions. The crystal structure of the title compound was determined by X-ray analysis using counter data. The compound crystallizes in the triclinic system, space group* $P\bar{1}$, *with* a = *10.26(1),* b = *12.91(1),* c = *16.73(1) Å,* α = *111.27(3)°,* λ = *75.78(3)°, and* γ = *107.12(3)° for* Z = *2. The structure was refined to* R = *0.049. The rhenium atom is in a distorted octahedral co-ordination with two axial* PPh_3, *two* cis-*CO groups, and the bidentate ligand forming a four-membered ring with the metal.*

Introduction

Our recent investigations concern reactions of pseudo-allyl ligands, as triazenido-, $[RN{=}N{-}NR]^-$, and amidino $[RN{-}CR{=}NR]^-$, with rhenium complexes in various oxidation states.

In previous papers [1, 2] we reported the synthesis and characterization of new formamidino- and triazenido-complexes of Re^I of the type $[Re(CO)_2(RN\overset{..}{-}X\overset{..}{-}NR)(PPh_3)_2]$ (X = CH or N) having a pseudo-octahedral geometry with the chelate organonitrogen ligand and the CO groups in the equatorial plane. We reported also the synthesis of new Re^{III} complexes of the type $[ReCl_2(RN\overset{..}{-}N\overset{..}{-}NR)(PPh_3)_2]$ and the crystal structure of $[ReCl_2(p\text{-}MeC_6H_4N\overset{..}{-}N\overset{..}{-}NC_6H_4Me\text{-}p)(PPh_3)_2]$ [3]. Lately [4], the reaction of $ReOCl_3(PPh_3)_2$ with the formamidino ligand $C_6H_5NH{-}CH{=}NC_6H_5$ has led to the preparation of the arylimido-rhenium(V) complex $[Re(NAr)Cl_3(PPh_3)_2]$, which is a new route to the synthesis of this class of compounds [5].

Here, we report the synthesis and characterization of arylformamidorhenium(I) complexes of the type $[Re(CO)_2(ArN\overset{..}{-}CH\overset{..}{-}O)(PPh_3)_2]$ and the crystal structure of $[Re(CO)_2(p\text{-}NO_2C_6H_4N\overset{..}{-}CH\overset{..}{-}O)(PPh_3)_2]$.

Results and Discussion

The IR spectra of the complexes show two $\nu(C{=}O)$ in the 1925–1908 and 1850–1820 cm^{-1} ranges, which suggests a *cis* geometry (Table I). Variation of the *para* substituents in the phenyl ring causes small changes in the $\nu(C{=}O)$. Substitution of Cl^- and CO ligands with $[O\overset{..}{-}CH\overset{..}{-}NAr]^-$ causes a marked lowering in the $\nu(C{=}O)$ values (in $Re(CO)_3(PPh_3)_2Cl$ $\nu(C{=}O)$ appears at 2045w, 1940s, and 1885 cm^{-1} [6]). Analogous lowering was observed in the corresponding rhenium(I) complexes with triazenido and amidino ligands [1].

All the complexes are diamagnetic both in the solid state and in solution. This is consistent with an octahedral d^6 system in a strong ligand field causing a low spin configuration [7].

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TABLE I. Analytical and Spectroscopic Data.

Compound		M.p. (°C)	Colour	Yield	Analysis: Found (calc.) (%)			IR (cm^{-1}) Nujol		^1H NMR ($CDCl_3$) τ			
					C	H	N	$\nu(C{\equiv}O)$	$(ArN\overset{..}{-}CH\overset{..}{-}O)^a$	N-Aryl protons	CH	CH_3	OCH_3
I	$[Re(CO)_2(p\text{-}CH_3C_6H_4NCHO)(PPh_3)_2]$	170 (dec)	pale yellow	35	61.28 (61.31)	4.28 (4.25)	1.46 (1.55)	1910vs 1830vs	1550s, 1285s	3.52(m)	1.72(m)	7.77(s)	
II	$[Re(CO)_2(C_6H_5NCHO)(PPh_3)_2]$	242 (dec)	pale yellow	38	61.33 (60.93)	4.25 (4.09)	1.38 (1.58)	1925vs 1840vs	1540s, 1280s	3.40(m)	1.65(m)		
III	$[Re(CO)_2(p\text{-}ClC_6H_4NCHO)(PPh_3)_2]$	215 (dec)	pale yellow	35	58.84 (58.66)	3.88 (3.82)	1.40 (1.52)	1910vs 1830vs	1540s, 1290s	3.46(m)	1.67(m)		
IV	$[Re(CO)_2(p\text{-}CH_3OC_6H_4NCHO)(PPh_3)_2]$	214 (dec)	pale yellow	37	60.28 (60.26)	4.37 (4.18)	1.31 (1.53)	1908vs 1820vs	1540s, 1280s	3.63(m)	1.76(m)		6.27(s)
V	$[Re(CO)_2(p\text{-}NO_2C_6H_4NCHO)(PPh_3)_2]$	204 (dec)	yellow orange	45	58.06 (58.00)	3.88 (3.78)	2.99 (3.00)	1925vs 1850vs	1590s, 1280s	3.00(m)	1.48(m)		
VI	$[Re(CO)_2(o\text{-}CH_3C_6H_4NCHO)(PPh_3)_2]$	165 (dec)	pale yellow	45	60.76 (61.31)	4.63 (4.25)	1.39 (1.55)	1915vs 1835vs	1530s, 1280s	3.35(m)	1.70(m)	8.58(s)	

[a] Only bands associated with the arylformamido-linkages.

The ^1H NMR spectra (Table I) show the CH proton as a poorly resolved multiplet [downfield with respect to that of the free ligand which appears as a singlet] owing to the ^{31}P–H coupling of the methyne proton with the phosphine groups. The same coupling was observed in formamidino–phosphine complexes of molybdenum and tungsten [8].

X-Ray Structure of $[Re(CO)_2(p\text{-}NO_2C_6H_4N\overset{..}{-}CH\overset{..}{-}O)(PPh_3)_2]$

The structure consists of discrete molecules of the complex. Figure 1 shows the conformation of the molecule and the numbering scheme used throughout this paper. Final atomic coordinates are listed in Table II, bond distances and angles in Table III. Distortions from the idealized octahedral geometry arising from the constraints of the bidentate ligand are mainly localized in the base plane where it subtends an angle of only 59° at the metal atom. Atoms of the equatorial plane O(3), N(1), C(3), C(1), C(2) are very close to the best least-squares plane $4.159x + 7.190y + 6.985z = 5.890$ Å. The plane equation is referred tc the crystal axes with x, y, z as fractional coordinates. Atomic displacements from the plane are 0.02, –0.02, 0.02, –0.02, –0.005 Å for atoms O(3), N(1), C(3), C(1) and C(2), and –0.001 Å for Re, which was not used in the plane calculation. The phenylene ring is approximately coplanar with the equatorial plane being tilted of only 13.5° with respect to this plane. A small deviation from linearity of the axial substituents is also observed. The structure of $Re(CO)_2(p\text{-}NO_2C_6H_4N\overset{..}{-}CH\overset{..}{-}O)(PPh_3)_2$ (*I*) strictly resembles that [9] of $Re(CO)_2(PhN\overset{..}{-}CH\overset{..}{-}NPh)(PPh_3)_2$ (*II*) and that [2] of $[Re(CO)_2(p\text{-}MeC_6H_4N\overset{..}{-}N\overset{..}{-}NC_6H_4Me\text{-}p)(PPh_3)_2]$ (*III*) in which the N–Re–N angles are 60(1)° and 57(1)°. The Re–P and Re–C bond distances are fully comparable in all these compounds; the Re–N of 2.22(1) Å in (*I*) has the same value as the two Re–N bonds in (*II*) and is of the same order as found in (*III*) (mean 2.20 Å). The partial double bond character of the N(1)–C(3) distance [1.34(1) Å, compared with a mean of 1.33 Å in (*II*)] and of the C(3)–O distance, and the near planarity of the Re–N(1)–CH–O system suggest the presence of an extended π-conjugation in the base plane. As expected the Re^I–N and Re^I–P bond distances in (*I*), (*II*) and (*III*) [Re^I–N 2.21 Å (mean); Re^I–P 2.43 Å (mean)] are respectively longer and shorter than the corresponding distances in a similar Re^{III} compound [3] [Re^{III}–N 1.99(3), 2.08(2) Å; Re^{III}–P 2.50(1), 2.51(1) Å]. Bond lengths and angles in the nitro group are rather asymmetric, the O–N–O angle opposite to the C–N single bond being significantly larger and the C–N–O(4) angle opposite to the N=O(5) double bond being significantly narrower than 120°. However the observed asymmetry in the angles at N(2) is partially compensated from a similar

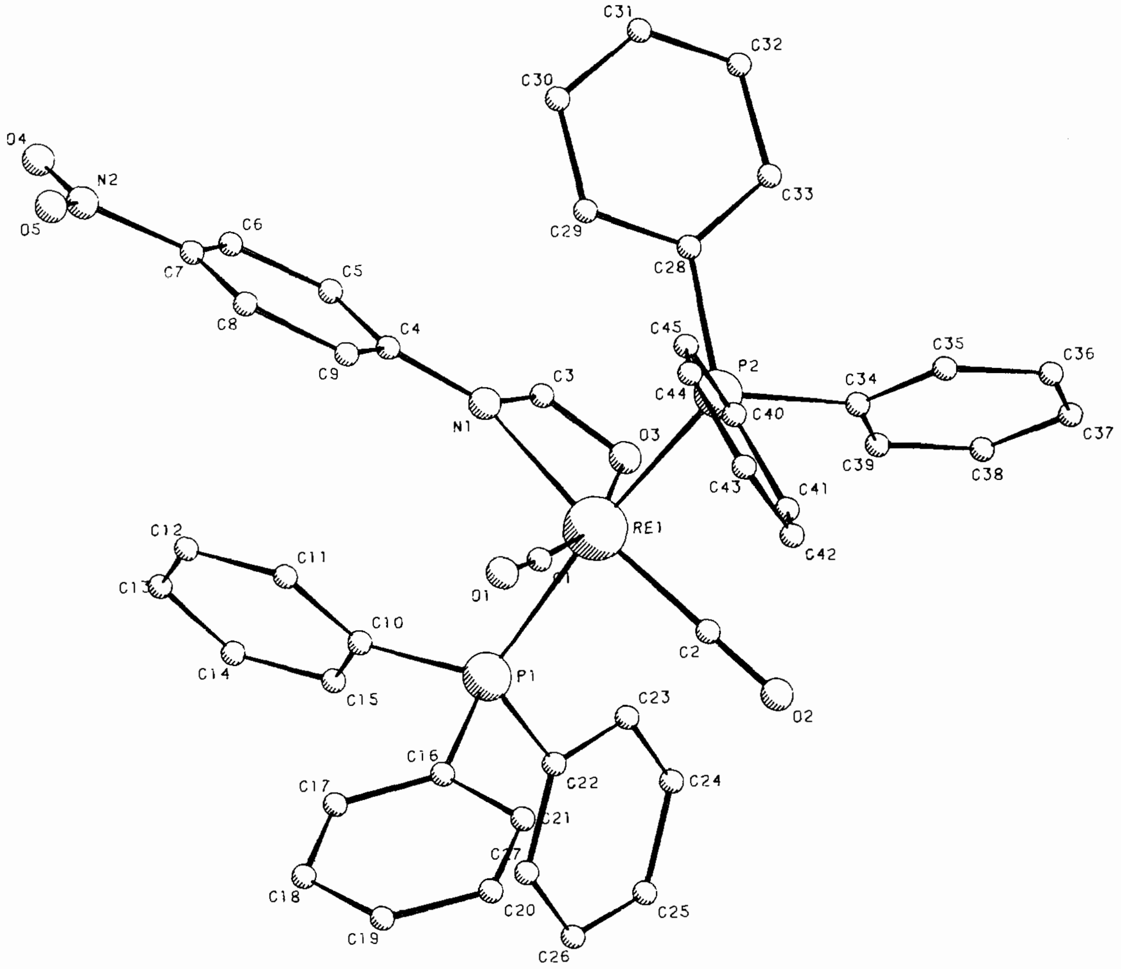

Fig. 1. Molecular structure of $[\mathrm{Re(CO)_2}(p\text{-}\mathrm{NO_2C_6H_4N{\cdots}CH{\cdots}O})(\mathrm{PPh_3})_2]$ with the numbering scheme.

TABLE II. Atomic Coordinates and Temperature Factors (Å^2).

Atom	X	Y	Z	U
Re	0.26442(3)	0.43957(3)	0.23322(2)	*
P(1)	0.1493(2)	0.2647(2)	0.1351(1)	*
P(2)	0.3857(2)	0.6226(2)	0.3190(2)	*
O(1)	0.5250(8)	0.3484(7)	0.1811(5)	*
O(2)	0.3429(9)	0.5378(7)	0.0827(5)	*
O(3)	0.0647(6)	0.4882(6)	0.3050(4)	*
O(4)	0.0788(12)	0.0800(10)	0.5803(8)	0.127(4)
O(5)	0.2939(12)	0.0833(9)	0.5229(7)	0.116(3)
N(1)	0.1553(7)	0.3873(6)	0.3492(5)	*
N(2)	0.1873(13)	0.1082(10)	0.5336(8)	0.093(3)
C(1)	0.4246(10)	0.3832(7)	0.1983(6)	*
C(2)	0.3139(10)	0.5000(8)	0.1393(7)	*
C(3)	0.0519(9)	0.4379(9)	0.3608(7)	*
C(4)	0.1605(9)	0.3240(8)	0.3999(6)	0.047(2)
C(5)	0.0455(12)	0.2893(10)	0.4592(8)	0.064(3)
C(6)	0.0553(11)	0.2187(9)	0.5022(7)	0.070(3)

(continued overleaf)

TABLE II. *(continued)*

Atom	X	Y	Z	U
C(7)	0.1762(10)	0.1862(9)	0.4876(7)	0.064(2)
C(8)	0.2932(10)	0.2194(8)	0.4328(7)	0.059(2)
C(9)	0.2831(10)	0.2897(8)	0.3868(6)	0.053(2)
C(10)	0.0349(8)	0.1549(7)	0.1811(5)	0.035(2)
C(11)	0.0875(9)	0.1193(8)	0.2335(6)	0.048(2)
C(12)	0.0063(10)	0.0357(8)	0.2703(6)	0.051(2)
C(13)	−0.1290(10)	−0.0145(8)	0.2544(6)	0.056(2)
C(14)	−0.1807(10)	0.0201(9)	0.2017(7)	0.058(2)
C(15)	−0.1013(9)	0.1056(8)	0.1658(6)	0.049(2)
C(16)	0.2699(8)	0.1860(7)	0.0504(5)	0.037(2)
C(17)	0.2614(9)	0.0718(7)	0.0349(6)	0.045(2)
C(18)	0.3582(10)	0.0155(9)	−0.0279(7)	0.058(2)
C(19)	0.4631(10)	0.0754(9)	−0.0763(7)	0.060(3)
C(20)	0.4705(10)	0.1893(8)	−0.0632(6)	0.056(2)
C(21)	0.3741(9)	0.2460(8)	0.0000(6)	0.047(2)
C(22)	0.0388(9)	0.2805(7)	0.0715(6)	0.044(2)
C(23)	−0.0370(12)	0.3653(10)	0.1103(8)	0.073(3)
C(24)	−0.1331(15)	0.3718(12)	0.0648(10)	0.094(4)
C(25)	−0.1462(12)	0.2954(10)	−0.0197(8)	0.068(3)
C(26)	−0.0725(10)	0.2124(8)	−0.0559(6)	0.054(2)
C(27)	0.0209(9)	0.2040(8)	−0.0104(6)	0.048(2)
C(28)	0.3595(9)	0.6613(8)	0.4388(6)	0.048(2)
C(29)	0.3662(11)	0.5818(9)	0.4741(7)	0.064(3)
C(30)	0.6577(13)	0.3941(11)	0.4331(8)	0.079(3)
C(31)	0.3101(14)	0.7113(12)	0.6177(9)	0.085(4)
C(32)	0.3035(13)	0.7878(11)	0.5842(9)	0.082(4)
C(33)	0.3284(11)	0.7666(9)	0.4921(7)	0.65(3)
C(34)	0.3554(9)	0.7459(7)	0.3036(6)	0.043(2)
C(35)	0.4541(10)	0.8495(9)	0.3166(7)	0.059(3)
C(36)	0.4267(11)	0.9440(9)	0.3072(7)	0.064(3)
C(37)	0.3018(11)	0.9358(9)	0.2848(7)	0.062(3)
C(38)	0.2020(11)	0.8324(9)	0.2731(7)	0.059(3)
C(39)	0.2305(9)	0.7386(8)	0.2816(6)	0.050(2)
C(40)	0.5732(8)	0.6393(7)	0.2846(6)	0.042(2)
C(41)	0.6266(10)	0.6485(8)	0.2018(6)	0.055(2)
C(42)	0.7667(11)	0.6498(9)	0.1680(7)	0.062(3)
C(43)	0.8523(11)	0.6413(9)	0.2175(7)	0.063(3)
C(44)	0.7985(11)	0.6303(9)	0.2995(7)	0.065(3)
C(45)	0.6582(10)	0.6314(9)	0.3345(7)	0.057(2)

*Anisotropic temperature factors are in the form $T = \exp(-2\pi^2 \Sigma_i \Sigma_j h_i h_j a_i^* a_j^* U_{ij})$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	0.0327(2)	0.0358(2)	0.0400(2)	0.0004(1)	−0.0104(1)	0.0107(1)
P(1)	0.034(1)	0.034(1)	0.040(1)	0.001(1)	−0.012(1)	0.010(1)
P(2)	0.031(1)	0.038(1)	0.044(1)	0.001(1)	−0.011(1)	0.001(1)
O(1)	0.056(4)	0.085(6)	0.088(6)	0.029(4)	−0.005(4)	0.016(5)
O(2)	0.116(7)	0.069(5)	0.064(5)	−0.004(5)	−0.024(5)	0.039(4)
O(3)	0.052(4)	0.063(4)	0.059(4)	0.019(3)	−0.018(3)	0.018(4)
N(1)	0.037(4)	0.050(4)	0.045(4)	−0.001(3)	−0.008(3)	0.016(4)
C(1)	0.064(6)	0.043(5)	0.035(5)	0.009(4)	−0.001(4)	0.022(4)
C(2)	0.050(5)	0.048(5)	0.053(6)	0.004(4)	−0.015(4)	0.008(5)
C(3)	0.038(5)	0.057(6)	0.062(6)	0.003(4)	−0.012(4)	0.005(5)

(continued on facing page)

TABLE II. *(continued)*

Atom	X	Y	Z
H(11)	0.1847	0.1542	0.2448
H(12)	0.0451	0.0116	0.3083
H(13)	−0.1877	−0.0746	0.2807
H(14)	−0.2769	−0.0168	0.1890
H(17)	0.1853	0.0285	0.0688
H(18)	0.3519	−0.0669	−0.0378
H(19)	0.5330	0.0362	−0.1205
H(20)	0.5447	0.2314	−0.0989
H(21)	0.3793	0.3280	0.0091
H(23)	−0.0237	0.4206	0.1693
H(24)	−0.1907	0.4298	0.0923
H(25)	−0.2099	0.3020	−0.0533
H(26)	−0.0849	0.1572	−0.1151
H(27)	0.0742	0.1429	−0.0372
H(29)	0.2844	0.5661	0.5185
H(30)	0.7241	0.3431	0.4117
H(31)	0.2544	0.7087	0.6754
H(32)	0.2807	0.8617	0.6238
H(33)	0.3238	0.8244	0.4667
H(35)	0.5445	0.8559	0.3327
H(36)	0.4975	1.0178	0.3167
H(37)	0.2829	1.0030	0.2770
H(38)	0.1106	0.8264	0.2587
H(39)	0.1599	0.6647	0.2717
H(41)	0.5652	0.6542	0.1663
H(42)	0.8049	0.6568	0.1087
H(43)	0.9522	0.6431	0.1940
H(44)	0.8592	0.6215	0.3340
H(45)	0.6206	0.6266	0.3945
H(5)	−0.0422	0.3098	0.4707
H(6)	−0.0264	0.1928	0.5440
H(8)	0.3776	0.1940	0.4278
H(9)	0.3627	0.3137	0.3460

TABLE III. Bond Distances (Å) and Angles (Degrees).

Distances

Re–P(1)	2.425(2)	C(3)–O(3)	1.28(2)
Re–P(2)	2.424(2)	C(3)–N(1)	1.34(1)
Re–N(1)	2.21(1)	N(1)–C(4)	1.39(2)
Re–O(3)	2.28(2)	C(4)–C(9)	1.42(2)
Re–C(1)	1.87(1)	C(4)–C(5)	1.40(1)
Re–C(2)	1.89(1)	C(5)–C(6)	1.39(1)
P(1)–C(10)	1.83(1)	C(6)–C(7)	1.36(2)
P(1)–C(16)	1.84(1)	C(7)–C(8)	1.39(1)
P(1)–C(22)	1.83(1)	C(8)–C(9)	1.42(2)
P(2)–C(28)	1.85(1)	N(2)–C(7)	1.51(2)
P(2)–C(34)	1.82(1)	N(2)–O(4)	1.23(2)
P(2)–C(40)	1.84(1)	N(2)–O(5)	1.18(2)

(continued overleaf)

TABLE III. *(continued)*

Angles

a) Co-ordination. (The errors are less than 1°).

P(1)–Re–P(2)	174	P(2)–Re–N(1)	93
P(1)–Re–N(1)	93	P(2)–Re–O(3)	88
P(1)–Re–O(3)	93	P(2)–Re–C(1)	91
P(1)–Re–C(1)	89	P(2)–Re–C(2)	87
P(1)–Re–C(2)	87	N(1)–Re–O(3)	59
C(1)–Re–C(2)	91	N(1)–Re–C(1)	105
C(1)–Re–O(3)	164	O(3)–Re–C(2)	105
C(2)–Re–N(1)	164		

b) p-$NO_2C_6H_4N\overset{..}{-}CH\overset{..}{-}O$. (The errors are less than 1.5°).

O(3)–C(3)–N(1)	114	C(5)–C(6)–C(7)	119
Re–O(3)–C(3)	93	C(9)–C(8)–C(7)	116
Re–N(1)–C(3)	93	C(6)–C(7)–C(8)	125
Re–N(1)–C(4)	143	C(6)–C(7)–N(2)	119
C(3)–N(1)–C(4)	124	C(8)–C(7)–N(2)	116
C(5)–C(4)–C(9)	120	C(7)–N(2)–O(4)	113
C(4)–C(5)–C(6)	119	C(7)–N(2)–O(5)	119
C(4)–C(9)–C(8)	120	O(4)–N(2)–O(5)	128

c) CO. (The errors are less than 1°).

Re–C(1)–O(1)	176	Re–C(2)–O(2)	179

d) PPh_3[a]. (The errors are less than 1°).

Re–P(1)–C(10)	118	Re–P(2)–C(28)	120
Re–P(1)–C(16)	113	Re–P(2)–C(34)	115
Re–P(1)–C(22)	116	Re–P(2)–C(40)	110
C(10)–P(1)–C(16)	103	C(28)–P(2)–C(34)	102
C(10)–P(1)–C(22)	102	C(28)–P(2)–C(40)	105
C(16)–P(1)–C(22)	102	C(34)–P(2)–C(40)	102

[a] Ph group mean C–C = 1.40 Å, mean C–C–C = 120°.

asymmetry in the angles at C(7) so that the C(6)··· O(4) and C(8)···O(5) contact distances are very close.

Experimental

Solvents were purified and dried before use. The compounds ArNHCHO [10] and *trans*-[$Re(CO)_3(PPh_3)_2Cl$] [6] were prepared following literature methods. Other materials were reagent grade. All the syntheses were performed under nitrogen. IR and ^1H NMR spectra were recorded on Perkin-Elmer 577 and 80-MHz Bruker spectrometers respectively.

Preparation of [$Re(CO)_2(ArN\overset{..}{-}CH\overset{..}{-}O)(PPh_3)_2$]

The compound $Re(CO)_3(PPh_3)_2Cl$ (0.24 mmol) was added to a solution of Li($O\overset{..}{-}CH\overset{..}{-}NAr$) (0.72 mmol) (Ar = C_6H_5, p-$CH_3C_6H_4$, p-ClC_6H_4, p-$CH_3OC_6H_4$) in dry THF (60 cm^3) at room temperature, under nitrogen atmosphere. During refluxing the solution assumed a pale yellow colour. After two hours the mixture was filtered and then concentrated *in vacuo*. A yellow powder was obtained by adding EtOH to the solution. The solid was washed with H_2O, EtOH, dried, and crystallized from CH_2Cl_2/EtOH.

The compounds [$Re(CO)_2(ArN\overset{..}{-}CH\overset{..}{-}O)(PPh_3)_2$] (Ar = p-$NO_2C_6H_4$, o-$CH_3C_6H_4$) were prepared by the same procedure in dry toluene and with a large excess of ligand.

X-Ray Diffractometry

A well formed fragment of [$Re(CO)_2(p$-$NO_2C_6H_4N\overset{..}{-}CH\overset{..}{-}O)(PPh_3)_2$] with approximate dimensions 0.10 × 0.15 × 0.15 mm was mounted on the end of a glass fibre with epoxy-adhesive. Cell dimensions were determined on a Philips PW 1100 automatic diffractometer using graphite-monochromatized Mo-Kα radiation. Unit-cell parameters were obtained by least-squares refinement of 25 carefully determined medium-angle reflections.

Crystal data

$C_{45}H_{35}N_2O_5P_2Re$, M = 869, triclinic, a = 10.26(1), b = 12.91(1), c = 16.73(1) Å, α = 111.27(3)°, β = 75.78(3)°, γ = 107.12(3)°, U = 1950 Å^3, Z = 2, D_c = 1.48 g cm^{-3} for Z = 2, $F(000)$ = 868, λ(Mo-Kα) = 0.7107 Å, μ(Mo-Kα) = 24 cm^{-1}, space group $P\bar{1}$.

Data, up to θ = 25°, were collected by the θ–2θ step-scan method using Mo-Kα radiation, with a scan rate of 2° min^{-1}. Two standard reflections measured at intervals of 100 min were constant within counting statistics. Of the 6398 independent reflections measured, 5442 were significantly above background $[I \geqslant 3\sigma(I)]$ and were used in subsequent calculations. The data were corrected for Lp and for absorption [11].

Solution of the structure was achieved by standard heavy-atom methods. Refinement of scale-factor, positional, and thermal parameters converged to give a final agreement index R of 0.049 when the largest parameter shift in the last cycle was about 0.5σ. The structure was refined by full-matrix least squares, minimizing the function $\Sigma w \Delta F^2$ with w = 1. The ring hydrogen atoms were introudced in calculated positions (C–H = 0.98 Å, U_{iso} = 0.05 Å^2).

A final difference-Fourier map showed no significant residuals. Scattering factors for Re were from ref. 12, and those for P, O, N, C, and H from ref. 13. The Re scattering factor was corrected for anomalous dispersion with constant average values $\Delta f'$ = –1.598 and $\Delta f''$ = 7.232 for the real and imaginary components.

All calculations were done using the X-RAY program system [14].

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