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Reactions of the Dirhenium(II) Complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with Isocyanides. 13.[1] Identification of a New Structural Isomer of the Dirhenium Cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ and Its Isomerization Behavior. Structural Characterization of $(XylNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CNXyl)(\mu\text{-dppm})_2ReCl(CO)$

Wengan Wu, Phillip E. Fanwick, and Richard A. Walton*

Department of Chemistry, Purdue University, 1393 Brown Building,
West Lafayette, Indiana 47907-1393

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A yellow form of the dirhenium salts of the type $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]Y$ (Y = Cl, O_3SCF_3, PF_6, ReO_4) has been shown to have the μ-CNXyl-bridged structure $[(XylNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CNXyl)(\mu\text{-dppm})_2ReCl(CO)]^+$ on the basis of an X-ray crystal structure determination of its neutral paramagnetic congener. The Re−Re bond length in the structure of $Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2$ is 2.7155(9) Å, in accord with the presence of a formal Re−Re bond order of 1.5. This particular cation constitutes the fourth isomer of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ to have been structurally characterized.

Introduction

The ability of the triply bonded dirhenium(II) synthons $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) to react with carbon monoxide and organic isocyanides, with incorporation of up to three of these ligands into the coordination sphere of the dimetal unit, is well-established (see Table 1).[1−14] In several instances, these complexes have been shown to exist as structural isomers.[1,3−7,9,11] The scope of this chemistry is currently under investigation in our laboratory, a principle aim of which is to identify new classes and types of isomers in redox-active dimetal systems which contain metal−metal bonds.

One system which exemplifies the range of isomers that can be obtained is the mixed carbonyl−xylyl isocyanide dirhenium cation $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ (Xyl = xylyl),[1,4,5,11] which has been definitively identified in at least three distinct structural forms. In this communication, we report details of the structural characterization of a fourth isomer of this complex cation.

Experimental Section

Starting Materials and General Procedures. The yellow isomeric forms of the complex $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]Y$, viz. $[(XylNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CNXyl)(\mu\text{-dppm})_2ReCl(CO)]Y$ (Y = Cl (**1a**), O_3SCF_3 (**1b**), or PF_6 (**1c**)),[5,9] and the compounds $[(t\text{-}BuNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CNXyl)(\mu\text{-dppm})_2ReCl(CO)]PF_6$ (**8**)[7] and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$[15] were prepared according to literature procedures. 2,6-Dimethylphenyl isocyanide, XylNC, was purchased from Fluka Chemical, Corp., and $(\eta^5\text{-}C_5H_5)_2Co$ and *tert*-butyl isocyanide (*t*-BuNC) were purchased from Aldrich Chemical, Co. Solvents were obtained from commercial sources and were deoxygenated by purging with dinitrogen prior to use. All reactions were performed under an atmosphere of dry nitrogen. IR spectra, ^1H and $^{31}P\{^1H\}$ NMR spectra, and cyclic voltammetric measurements were determined as described previously.[4,6] Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

A. Synthesis of $(XylNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CNXyl)(\mu\text{-dppm})_2ReCl(CO)$ (6). (i) From $[(XylNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CNXyl)(\mu\text{-dppm})_2ReCl(CO)]Cl$ (1a). A sample of **1a** (16.5 mg, 0.0105 mmol) was reacted with 2.5 mg of $(\eta^5\text{-}C_5H_5)_2Co$ (0.0132 mmol) in 8 mL of dichloromethane for 1 h. A green solution formed during this period. The reaction mixture was filtered to remove any insoluble material, and the volume of the filtrate was reduced to ca. 1 mL. An equal volume of diethyl ether was then added, a yellow precipitate of $[(\eta^5\text{-}C_5H_5)_2Co]Cl$ was filtered off, and the filtrate was evaporated under a stream of dinitrogen to yield the title complex **6**; yield 15.3 mg (95%). Anal. Calcd for $C_{69}H_{62}Cl_3N_2OP_4Re_2$: C, 53.89; H, 4.06; N, 1.82.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

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Table 1. Typical Products from the Reactions of $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl or Br) with CO and Organic Isocyanides

complex type	ligand sets	refs
$Re_2X_4(\mu\text{-dppm})_2L$	L = CO, *t*-BuNC, or XylNC	6,10,11,14
$Re_2X_4(\mu\text{-dppm})_2L_2$	L = CO	14
$Re_2X_4(\mu\text{-dppm})_2LL'$	L = CO, L′ = *i*-PrNC, *t*-BuNC, XylNC, or MesNC	4,6,11
$[Re_2X_3(\mu\text{-dppm})_2L_3]^+$	L = CO, *t*-BuNC or XylNC	8,12
$[Re_2X_3(\mu\text{-dppm})_2L_2L']^+$	L = CO, L′ = *i*-PrNC, *t*-BuNC, or XylNC L = *t*-BuNC or XylNC, L′ = CO	1−5, 7,9,13
$[Re_2X_3(\mu\text{-dppm})_2LL'L'']^+$	L = CO, L′ = *t*-BuNC, L″ = XylNC	2,7

Table 2. Crystallographic Data for the Complex $Re_2(\mu\text{-Cl})(\mu\text{-CNXyl})(\mu\text{-dppm})_2Cl_2(CO)(CNXyl)$ (6)

empirical formula	$Re_2Cl_3P_4ON_2C_{69}H_{62}$	*Z*	4
fw	1537.93	ρ_{calcd}, g/cm^3	1.633
space group	$P2_1/n$ (No. 14)	μ, cm^{-1} (Mo Kα)	41.93
a, Å	19.058(3)	trans. factors, min/max	0.46/0.94
b, Å	15.505(4)	data with $I > 3.0\sigma(I)$	5276
c, Å	21.274(3)	R^a/R_w^b	0.037/0.043
β, deg	95.723(14)	largest shift/error	0.01
V, Å^3	6255(4)	GOF^c	0.552

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Goodness-of-fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

Found: C, 53.60; H, 3.84, N, 1.93. IR (ν, cm^{-1}): 2086 (vs), 1942 (vs), 1618 (m-w), 1570 (m).

(ii) From $[(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CNXyl})(\mu\text{-dppm})_2ReCl(CO)]O_3SCF_3$ (1b). The reaction procedure and workup are very similar to those described in section A(i), except that a longer reaction time (5 h) was used; yield 82%.

B. Oxidation of $(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CNXyl})(\mu\text{-dppm})_2ReCl(CO)$ (6) to $[(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CNXyl})(\mu\text{-dppm})_2ReCl(CO)]PF_6$ (1c). A mixture of **6** (15.0 mg, 0.0098 mmol) and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (3.5 mg, 0.0106 mmol) was treated with 6 mL of dichloromethane at 25 °C. The resulting solution was stirred for 30 min, during which time a color change from green to orange was observed. The reaction solution was reduced to ca. 0.5 mL, and 5 mL of diethyl ether was added to induce precipitation of the product. The complex $[(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CNXyl})(\mu\text{-dppm})_2ReCl(CO)]PF_6$ (**1c**) was collected as a yellow-orange solid by filtration; yield 15.5 mg (94%). The identification of this product was based upon its spectroscopic properties, which were identical to those observed for samples of this same complex prepared as described in ref 5.

C. Reaction of $[(t\text{-BuNC})ClRe(\mu\text{-Cl})(\mu\text{-CNXyl})(\mu\text{-dppm})_2ReCl(CO)]PF_6$ (8) with XylNC. A mixture of **8** (56.0 mg, 0.0343 mmol) and XylNC (4.5 mg, 0.0343 mmol) was dissolved in 20 mL of 1,2-dichloroethane, and the solution was heated at reflux for 20 h. A green solution formed during this period, which upon evaporation and work-up afforded the green isomer $[(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2ReCl(CNXyl)]PF_6$ (**3**); yield 53.0 mg (92%). This product was characterized by comparison of its spectroscopic properties with the literature data for this complex.[5]

D. Reaction of $[(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CNXyl})(\mu\text{-dppm})_2ReCl(CO)]PF_6$ (1c) with *t*-BuNC. A sample of **1c** (20.0 mg, 0.0119 mmol) was mixed with *t*-BuNC (2.0 μL, 0.0179 mmol) in 20 mL of 1,2-dichloroethane, and the resulting solution was heated at reflux for 22 h. A green solution formed during this period, and a mixture of $[(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2ReCl(CNXyl)]PF_6$ (**3**) and $[(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2ReCl(CN\text{-}t\text{-Bu})]PF_6$ (**9**) (product ratio **3**:**9** ≈ 7:3) was obtained following evaporation of the reaction solvent; yield 18.5 mg (93%).

E. Attempted Reaction of $[(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2ReCl(CNXyl)]PF_6$ (3) with *t*-BuNC. A sample of **3** (45.0 mg, 0.0267 mmol) was mixed with *t*-BuNC (3.0 μL, 0.0265 mmol) in 30 mL of 1,2-dichloroethane. The resulting solution was heated at reflux for 24 h. No reaction was found to occur, and the starting complex **3** was recovered unchanged.

F. Reaction of $[(t\text{-BuNC})ClRe(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2ReCl(CNXyl)]PF_6$ (9) with XylNC. A mixture of **9** (45.0 mg, 0.0275 mmol) and XylNC (4.0 mg, 0.0305 mmol) was heated in 30 mL of 1,2-dichloroethane at reflux for 24 h. No reaction was observed to occur during this period, and the starting complex **9** was recovered unchanged.

G. Attempted Isomerization of Compound 6 to a CO-Bridged Isomer. A solution of **6** (18.5 mg, 0.0118 mmol) in 1,2-dichloroethane (15 mL) was refluxed for 16 h. A standard work-up afforded unreacted starting material in essentially quantitative yield.

X-ray Crystallography. Single crystals of compound **6** suitable for X-ray diffraction analysis were grown from a solution in $CH_2Cl_2/CH_3C(O)OC_2H_5$ (1/1) by slow evaporation of the solvents at 25 °C. A dark green plate of **6** having approximate dimensions of 0.26 × 0.25 × 0.05 mm was mounted on a glass fiber in a random orientation. The data collection was performed on an Enraf-Nonius CAD4 computer controlled diffractometer with graphite-monochromatized Mo Kα radiation at 295 K. The cell constants were based on 25 reflections obtained in the range of $16° < \theta < 20°$, measured by the computer-controlled diagonal slit method of centering. Calculations were performed on an AlphaServer 2100 computer by use of the MolEN[16] structure determination package. Lorentz and polarization corrections were applied to the data set. An empirical absorption correction[17] was also applied, but no correction for extinction was made.

Compound **6** crystallized in the monoclinic crystal system. The systematic absences observed on the data set were consistent with a space group $P2_1/n$, Table 2. The structure was solved by a combination of direct methods (SHELXS-86)[18] and difference Fourier syntheses. All non-hydrogen atoms in this structure were refined anisotropically. The hydrogen atoms were calculated according to the idealized geometries with C−H = 0.95 Å and $\mathbf{U}(H) = 1.3\mathbf{U}_{eq}(C)$. Their contributions were added to the structure factor calculations, but their positions were not refined. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where *w* is the weighting factor defined as $w = 1/\sigma^2(|F_o|)$. Corrections for anomalous scattering were applied to the anisotropically refined atoms.[19] The final residuals for **6** were $R = 0.037$ and $R_w = 0.043$ with GOF = 0.552. The highest peak in the final difference Fourier was 1.23 e/Å^3.

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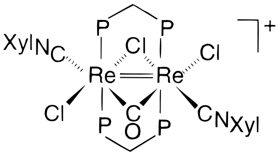
Results and Discussion

Background. The yellow isomeric form of the salts $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]Y$ (Y = Cl (**1a**), O_3SCF_3 (**1b**), PF_6 (**1c**), ReO_4 (**1d**))[5,9] has previously been assigned the edge-sharing bioctahedral structure as depicted in structure **1**, based upon the similarity of the spectroscopic and electrochemical properties of these salts to those of analogous bis(carbonyl)−monoisocyanide complexes of composition $[Re_2Cl_3(\mu\text{-dppm})_2(CO)_2(CNR)]Y$ (R = *i*-Pr, *t*-Bu, Xyl),[9,13] the structures of which have been established by X-ray crystallography (structure **2**). *This assignment of the structure of **1** is now known to be incorrect (vide infra).*



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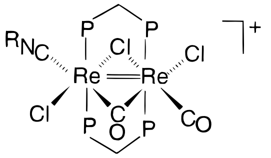
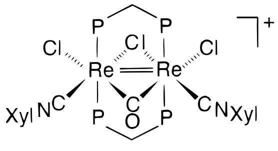


2

In addition to the yellow isomeric form of $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$, both green (structure **3**)[5] and orange-brown (structure **4**)[4] isomers have been synthesized and characterized by X-ray crystallography. Furthermore, we have recently shown[1] that the isomer which possesses structure **4** converts to structure **5** upon heating in 1,2-dichloroethane; *the latter isomeric form possesses no metal−metal bond.*



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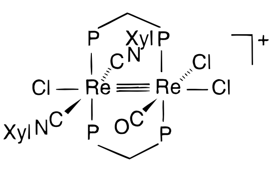

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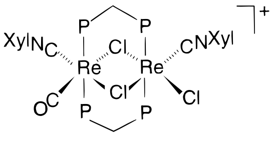
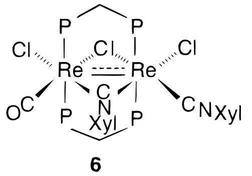


5

In spite of many attempts to obtain good quality single crystals of the yellow isomer **1** for an X-ray crystal structure determination, so as to confirm or refute the earlier structural formulation (structure **1**),[5,9] we have not yet been successful. However, by reducing **1** to its neutral congener $Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2$, **6**, we have now succeeded in obtaining a species that we have been able to identify structurally.



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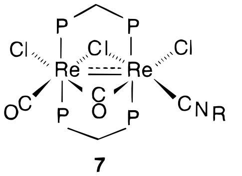

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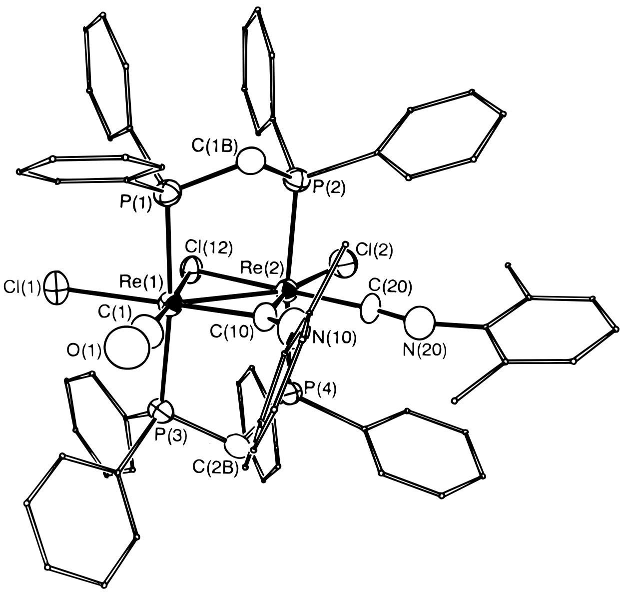

Figure 1. ORTEP[20] representation of the dirhenium complex $(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CNXyl})(\mu\text{-dppm})_2ReCl(CO)$ (**6**). The thermal ellipsoids are drawn at the 50% probability level, except for the phenyl group atoms of the dppm ligands and the xylyl group atoms of the XylNC ligand which are circles of arbitrary radius.

Synthesis and Characterization of $Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2$ (6). The cyclic voltammograms of solutions of the yellow salts $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]Y$ (**1a**−**d**) in 0.1 M TBAH/CH_2Cl_2 show three reversible processes, which correspond to a one-electron oxidation and two one-electron reductions of the bulk complexes.[5] The first reduction, characterized by an $E_{1/2}$ value of ca. −0.10 V vs Ag/AgCl, can be accessed chemically by cobaltocene. The treatment of dichloromethane solutions of complexes **1a** (Y = Cl) and **1b** (Y = O_3SCF_3) with stoichiometric amounts of $(\eta^5\text{-}C_5H_5)_2Co$ affords the green neutral complex $Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2$ (**6**). Its cyclic voltammetric properties, which are identical to those of **1a**−**d**, and its conversion to the salt $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]PF_6$ (**1c**), upon treatment with the one-electron oxidant $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in dichloromethane, confirms its close structural relationship to **1**. This is further supported by a comparison of the IR spectroscopic properties of **1** and **6**. The three bands which are found in the ranges 2140−2136 (s), 2004−2002 (s), and 1701−1664 (m-w,br) cm^{-1} in the IR spectra of the various salts of **1** are assignable[5] to the $\nu(CO)$ and $\nu(CN)$ modes of the dirhenium cation. These bands shift to 2086 (vs), 1942 (vs) and ~1620 (m,br) cm^{-1}, respectively, upon reduction to the neutral congener **6**, in accord with a more highly reduced dimetal core and, consequently, an increase in metal → $CO(\pi^*)$ and metal → $RNC(\pi^*)$ back-bonding. In contrast to the diamagnetism of **1**,[5] the reduced complex **6** is paramagnetic as shown by the presence of very broad and poorly defined resonances in the ^1H NMR spectrum and a magnetic moment measurement of $1.7 \pm 0.2\ \mu_B$, as determined by the Evans method in chloroform.

The stereochemistry of **6** has been confirmed by X-ray crystallography. An ORTEP[20] representation of the structure is shown in Figure 1, and important bond distances and angles are given in Table 3. The structure is that of an edge-sharing bioctahedron (structure **6**), with a bridging XylNC ligand and *not a bridging CO*

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[20] Johnson, C. K. ORTEP II, Report ORNL-5138; Oak Ridge National Laboratory: TN, 1976.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for the Complex $Re_2(\mu\text{-}Cl)(\mu\text{-}CNXyl)(\mu\text{-}dppm)_2Cl_2(CO)(CNXyl)$ (6)[a]

Distances			
Re(1)−Re(2)	2.7155(9)	Re(2)−P(2)	2.443(4)
Re(1)−Cl(1)	2.462(5)	Re(2)−P(4)	2.430(4)
Re(1)−Cl(12)	2.477(4)	Re(2)−C(10)	2.069(16)
Re(1)−P(1)	2.437(4)	Re(2)−C(20)	1.970(18)
Re(1)−P(3)	2.475(4)	O(1)−C(1)	1.13(2)
Re(1)−C(1)	1.914(18)	N(10)−C(10)	1.23(2)
Re(1)−C(10)	2.174(15)	N(10)−C(11)	1.43(2)
Re(2)−Cl(2)	2.440(5)	N(20)−C(20)	1.15(2)
Re(2)−Cl(12)	2.478(4)	N(20)−C(21)	1.42(2)

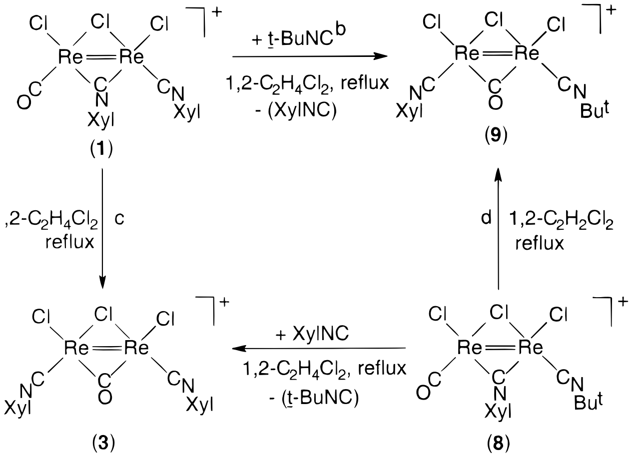
Angles			
Re(2)−Re(1)−Cl(1)	146.91(10)	C(1)−Re(1)−C(10)	78.2(7)
Re(2)−Re(1)−Cl(12)	56.79(9)	Re(1)−Re(2)−Cl(2)	146.82(11)
Re(2)−Re(1)−P(1)	93.21(11)	Re(1)−Re(2)−Cl(12)	56.75(9)
Re(2)−Re(1)−P(3)	91.81(10)	Re(1)−Re(2)−P(2)	93.64(11)
Re(2)−Re(1)−C(1)	126.7(5)	Re(1)−Re(2)−P(4)	95.32(10)
Re(2)−Re(1)−C(10)	48.5(4)	Re(1)−Re(2)−C(10)	51.9(4)
Cl(1)−Re(1)−Cl(12)	90.30(13)	Re(1)−Re(2)−C(20)	129.0(6)
Cl(1)−Re(1)−P(1)	84.00(15)	Cl(2)−Re(2)−Cl(12)	90.08(14)
Cl(1)−Re(1)−P(3)	89.71(15)	Cl(2)−Re(2)−P(2)	85.52(15)
Cl(1)−Re(1)−C(1)	86.2(6)	Cl(2)−Re(2)−P(4)	84.71(15)
Cl(1)−Re(1)−C(10)	163.4(4)	Cl(2)−Re(2)−C(10)	161.1(4)
Cl(12)−Re(1)−P(1)	92.46(14)	Cl(2)−Re(2)−C(20)	84.2(6)
Cl(12)−Re(1)−P(3)	87.11(14)	Cl(12)−Re(2)−P(2)	90.64(14)
Cl(12)−Re(1)−C(1)	176.4(6)	Cl(12)−Re(2)−P(4)	90.81(14)
Cl(12)−Re(1)−C(10)	105.3(4)	Cl(12)−Re(2)−C(10)	108.6(4)
P(1)−Re(1)−P(3)	173.69(15)	Cl(12)−Re(2)−C(20)	174.1(6)
P(1)−Re(1)−C(1)	86.9(5)	P(2)−Re(2)−P(4)	170.13(14)
P(1)−Re(1)−C(10)	89.7(4)	P(2)−Re(2)−C(10)	91.6(4)
P(3)−Re(1)−C(1)	93.1(5)	P(2)−Re(2)−C(20)	90.4(5)
P(3)−Re(1)−C(10)	96.5(4)	P(4)−Re(2)−C(10)	97.2(4)
P(4)−Re(2)−C(20)	87.1(5)	Re(1)−C(1)−O(1)	174.4(18)
C(10)−Re(2)−C(20)	77.1(7)	Re(1)−C(10)−Re(2)	79.5(5)
Re(1)−Cl(12)−Re(2)	66.45(10)	Re(1)−C(10)−N(10)	141.4(13)
C(10)−N(10)−C(11)	143.3(17)	Re(2)−C(10)−N(10)	138.7(13)
C(20)−N(20)−C(21)	167.0(19)	Re(2)−C(20)−N(20)	175.7(16)

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

as previously proposed (see structure **1**).[5,9] Furthermore, this isomeric form possesses an all-cis arrangement of π-acceptor ligands. The Re−Re bond distance for **6** is 2.7155(9) Å; this value is in accord with a metal−metal bond order of 1.5, which would be expected[9] upon the one-electron reduction of the doubly bonded cationic species **1**. The Re−Re distance for **6** is essentially identical to the value of 2.718(1) Å which has been reported[9] for the neutral complex $Re_2Cl_3(\mu\text{-}dppm)_2(CO)_2(CN\text{-}i\text{-}Pr)$, **7**; the latter complex is an edge-sharing bioctahedron (structure **7**), with a μ-CO ligand rather than μ-CNR. Complexes **6** and **7** can be expected to possess very similar electronic properties.

The bridging chloro ligand Cl(12) and the carbon atom C(10) of the bridging XylNC ligand of **6** are bound symmetrically to the two Re centers. While the Re−Cl and Re−C distances associated with these ligands are expected to be a little longer than those involving the terminal ligands Cl(1), Cl(2), and C(20), this is not apparent within the limits of 3σ (Table 3). The angles Re(1)−C(10)−N(10) and Re(2)−C(10)−N(10) are very similar (141.4(13)° and 138.7(13)°, respectively) and again support a symmetrical bonding mode for the μ-CNXyl ligand, while a distance of 1.23(2) Å for C(10)−N(10) reflects a reduction in the C−N bond order of this ligand to somewhere between 3 and 2. This distance can be compared to that for the corresponding C−N bond in the terminally bound XylNC ligand of **6** (C(20)−N(20) = 1.15(2) Å), in which the bond order is closer to 3. Note that the μ-iminyl ligand in the dirhenium complex $[Re_2Cl_3(\mu\text{-}dppm)_2(\mu\text{-}CNH\text{-}t\text{-}Bu)(CN\text{-}t\text{-}Bu)_2]PF_6$[12] possesses a formal C−N bond order of 2; in keeping with this, the C−N distance increases to 1.38(2) Å. The rehybridization which occurs upon formation of the μ-CNXyl ligand in **6** leads to a considerable bending at the sp^2 hybridized N atom; this is reflected by a value of 143.3(17)° for the angle C(10)−N(10)−C(11). For the terminal XylNC ligand, which approaches linearity, the angles Re(2)−C(20)−N(20) and C(20)−N(20)−C(21) are 175.7(16)° and 167.0(19)°, respectively. Many of the other structural parameters for **6** resemble those observed previously for other complexes of this general type, including the symmetrical all-cis isomer of $[Re_2Cl_3(\mu\text{-}dppm)_2(CO)(CNXyl)_2]^+$ which possesses structure **3**.[5]

Scheme 1. Reactions of Salts of the XylNC-Bridged Complexes $[(XylNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CNXyl)(\mu\text{-}dppm)_2ReCl(CO)]^+$ (1) and $[(t\text{-}BuNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CNXyl)(\mu\text{-}dppm)_2ReCl(CO)]^+$ (8) in the Presence and Absence of RNC Ligands[a]



[a] The μ-dppm ligands are omitted from the structural representations. [b] This reaction leads to appreciable quantities of **3**, in addition to **9** (product ratio for **9**:**3** = 3:7) because of the competitive reaction between *t*-BuNC and the dissociated XylNC ligand for the coordinatively unsaturated intermediate species $\{[Re_2Cl_3(\mu\text{-}dppm)_2(CO)(CNXyl)]^+\}$. [c] See refs 5 and 9. [d] See ref 7.

The structural identities of the yellow isomer, **1**, of the salts $[Re_2Cl_3(\mu\text{-}dppm)_2(CO)(CNXyl)_2]Y$ (i.e. possessing a structure closely related to that of **6**) and the green isomer **3** are in accord with our previous structural characterizations of the two edge-sharing bioctahedral isomers of the mixed-isocyanide ligand complexes $[Re_2Cl_3(\mu\text{-}dppm)_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]PF_6$.[7] A brown form $[(t\text{-}BuNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CNXyl)(\mu\text{-}dppm)_2ReCl(CO)]PF_6$ (**8**) and a green isomeric form $[(XylNC)ClRe(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CN\text{-}t\text{-}Bu)]PF_6$ (**9**) were identified, based upon an analysis of the IR spectral properties of isotopically labeled derivatives; **1** and **8** were shown to bear a very close structural relationship to one another, as do **3** and **9**.

The Isomerization Behavior of Yellow 1. The thermal isomerization of salts of the yellow isomer **1** to the corresponding green isomer **3** has been reported previously,[5,9] as has the isomerization of the brown XylNC-bridged isomeric form **8** of the mixed-isocyanide complex $[Re_2Cl_3(\mu\text{-}dppm)_2(CO)(CNXyl)(CN\text{-}t\text{-}Bu)]PF_6$ to the green CO-bridged isomer **9**.[7] These transformations are shown in Scheme 1. With the structure of **1** firmly established, we can consider the mechanism of this isomerization.

The aforementioned isomerizations appear to proceed via the dissociation of an isocyanide ligand from the isomers **1** and **8** and its subsequent recoordination to form the more thermodynamically stable isomers **3** and **9**, respectively (see Scheme 1). Thus, when a mixture of **8** and XylNC is heated in 1,2-dichloroethane, the *t*-BuNC ligand is displaced by XylNC and the stable CO-bridged isomer **3** is formed in essentially quantitative yield. An analogous reaction occurs when the $[PF_6]^-$ salt **1c** is heated with *t*-BuNC; the CO-bridged mixed-isocyanide ligand complex **9** is formed along with appreciable quantities of the analogous bis(XyNC) complex **3**. The product distribution (**9**:**3** $\approx$ 3:7) signifies that recoordination of the dissociated XylNC ligand is favored over that of the added *t*-BuNC ligand in these competitive reactions. The failure of the CO-bridged isomers **3** and **9** to react with *t*-BuNC and XylNC, respectively, confirms their kinetic stability.

When 1,2-dichloroethane solutions of the paramagnetic complex **6** (structurally analogous to **1**) are refluxed for periods of up to 16 h, *no isomerization* to the CO-bridged isomeric form is observed and **6** can be recovered quantitatively. We attribute the kinetic stability of **6** to the more tightly bound nature of the XylNC ligands, resulting from an enhanced degree of Re → XylNC(π^*) back-bonding in this more highly reduced complex.

Conclusions

The present study identifies a fourth structural isomer of the $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ cation (**1**) as one which possesses the μ-CNXyl-bridged structure $[(XylNC)ClRe(\mu\text{-Cl})(\mu\text{-CNXyl})(\mu\text{-dppm})_2ReCl(CO)]^+$. This conclusion is supported by a single-crystal X-ray structure determination of its one-electron reduced congener **6**. Earlier investigations[5,9] had incorrectly interpreted the IR spectra of the salts of **1**. Bands in the ranges 2140−2136 (s), 2004−2000 (s), and 1701−1664 (m-w,br) cm^{-1} were assigned[5,9] to $\nu(CN)_t$, $\nu(CN)_t$, and $\nu(CO)_b$ modes, respectively; the correct assignment is $\nu(CN)_t$, $\nu(CO)_t$, and $\nu(CN)_b$. The correct structural identification of **1** establishes a new type of isomer for dirhenium complexes which contain a metal−metal bonded $[Re_2(\mu\text{-dppm})_2]$ unit and have an edge-sharing bioctahedral geometry.

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Supporting Information Available: Full details for the crystal data and data collection parameters (Table S1), atomic positional parameters (Tables S2 and S3), anisotropic thermal parameters (Table S4), bond distances (Table S5), and bond angles (Table S6) for **6** (10 pages). Ordering information is given on any current masthead page.

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