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DIRHENIUM COMPLEXES CONTAINING LINKED DIPHENYLACETYLENE MOLECULES FROM THE PHOTOREACTION OF $H_3Re_3(CO)_{12}$ WITH PhC≡CPh. CRYSTAL AND MOLECULAR STRUCTURES OF $Re_2(CO)_5(C_4Ph_4)(C_2Ph_2)$ AND $Re_2(CO)_4(C_6Ph_6)(C_2Ph_2)\cdot\frac{1}{2}$ HEXANE

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Summary

Photolysis of $H_3Re_3(CO)_{12}$ in presence of diphenylacetylene (DPA) yields $Re_2(CO)_{10}$, $HRe(CO)_5$, and the three alkyne complexes $Re_2(CO)_7(DPA)_2$, $Re_2(CO)_5(C_4Ph_4)(DPA)$ (**4**) and $Re_2(CO)_4(C_6Ph_6)(DPA)$ (**3**), the latter two which were shown by X-ray crystallography to possess linked DPA ligands. The complex $Re_2(CO)_5(C_4Ph_4)(DPA)$ crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with *a* 11.277(3), *b* 12.301(3), *c* 14.851(3) Å, α 97.37(2), β 104.68(2), γ 104.49(2)°, *V* 1889(2) Å^3, and $Z = 2$. The structure was refined using the 4548 reflections with $I \geqslant 2\sigma(I)$ to give final residuals of $R = 0.031$ and $R_w = 0.041$. Complex **4** possesses a rhenacyclopentadiene group bonded to the second rhenium atom and an η^2-DPA ligand bound to the rhenium atom of the metallacycle. The complex $Re_2(CO)_4(C_6Ph_6)(DPA)$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with *a* 17.048(4), *b* 16.676(2), *c* 18.569(4) Å, β 106.70(2)°, *V* 5056(3) Å^3, and $Z = 4$. For the 3568 reflections with $I \geqslant 2\sigma(I)$, the structure refined to $R = 0.078$ and $R_w = 0.074$. Three of the DPA molecules in $Re_2(CO)_4(C_6Ph_6)(DPA)$ are linked together to form a "fly-over bridge" between the two rhenium atoms. The fourth DPA molecule is η^2-bound to one rhenium center.

In conjunction with an earlier study of the photochemical properties of $H_3Re_3(CO)_{12}$, we noted that irradiation of this cluster with diphenylacetylene (DPA) present led to a complex mixture of products [1]. On the basis of their IR and mass spectra, two of these new compounds were formulated as $H_2Re_2(CO)_7(DPA)_2$ and $H_2Re_2(CO)_5(DPA)_3$ but were not further characterized. Recently, Mays et al. [2] reported the formation of the dirhenium complexes $Re_2(CO)_7(DPA)_2$ (**1**), $Re_2(CO)_6(DPA)_3$ (**2**), and $Re_2(CO)_4(DPA)_4$ (**3**), from the thermal reaction of $Re_2(CO)_{10}$ with DPA. The structures **1**–**3** were suggested for these products.

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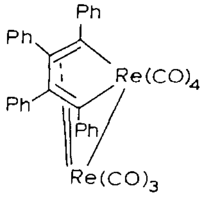
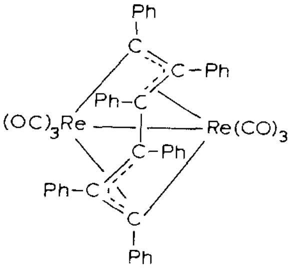


(1)



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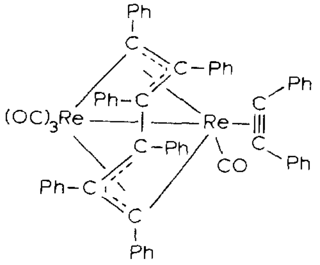
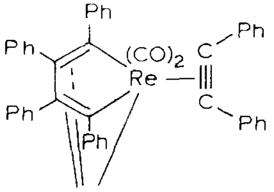


(3)

Considerable precedent [3] exists for the binuclear metallacyclic structure proposed for **1**, but no rhenacyclopentadiene compounds have been previously characterized via X-ray crystallographic analysis. A disorder problem prevented a complete structural determination for Mays et al. compound **3**. However, a partial analysis confirmed the chain of 3 linked acetylene molecules, but the location of the fourth DPA ligand was not established. However, its suggested formulation was supported by a crystal structure determination of an RNC derivative of it, $Re_2(CO)_4(C_6Ph_6)(RNC)_2$ ($R = CH_2SO_2C_6H_4CH_3$-*p*). Other C_6R_6 "fly-over bridged" compounds have been characterized [3e,4].

The study of Mays et al. [2] prompted us to reexamine the photoinduced reaction between $H_3Re_3(CO)_{12}$ and DPA to better characterize the photoproducts. This has led to the isolation and characterization of two new compounds whose crystal structures are described herein. The compound originally [1] thought to be $H_2Re_2(CO)_5(DPA)_3$ is now shown to be $Re_2(CO)_5(C_4Ph_4)(DPA)$ (**4**) without the hydride ligands but with two DPA's linked in a rhenacyclopentadiene ring.



(4)

Also characterized is $Re_2(CO)_4(C_6Ph_6)(DPA)$ which is identical to the formulation given by Mays et al. for their compound **3**. Both of these compounds possess one DPA ligand bound in an η^2-fashion to a single rhenium atom. These compounds **3** and **4** are the first structurally characterized complexes which have η^2-alkynes of any type bound to Re and complex **4** is the first structurally characterized rhenacyclopentadiene.

Experimental

$H_3Re_3(CO)_{12}$ was prepared by direct hydrogenation of $Re_2(CO)_{10}$ according to the published procedure [5]. Diphenylacetylene (99%) was purchased from Aldrich Chemical Co. and used without further purification. Reagent grade pentane and isooctane were distilled from sodium under H_2 prior to use. Irradiations were carried out using a 450 watt medium-pressure mercury vapor lamp (Hanovia) in a water cooled quartz jacket. IR specta were recorded on a Perkin–Elmer 580 IR spectrophotometer in n-hexane or CH_2Cl_2 solutions using a 0.1 mm cell equipped with NaCl windows. ^1H NMR spectra were recorded on a Brucker WH200 spectrometer using $CDCl_3$ (99%) solutions at 25 °C.

Irradiation of $H_3Re_3(CO)_{12}$ with DPA

In a typical experiment, $H_3Re_3(CO)_{12}$ (0.22 g, 0.29 mmol) and DPA (1.03 g, 5.8 mmol) were suspended in 30 ml dry, N_2-saturated pentane in a 40 ml pyrex Schlenk flask. This was placed in a water bath maintained at ~ 25 °C next to the Hanovia lamp. The reaction mixture was irradiated for 12 to 18 h with vigorous magnetic stirring during which time the suspension changed from colorless to orange. A pentane-insoluble yellow-orange precipitate was removed by filtration and washed twice with dry, N_2-saturated pentane. The orange filtrate was evaporated to dryness in vacuo to give an orange-red residue. The yellow precipitate and the orange-red residue were chromatographed separately on silica gel (Kieselgel 60, Merck). Elution of the former with hexane gave an inseparable mixture of $H_3Re_3(CO)_{12}$, $Re_2(CO)_{10}$, and DPA. Elution with 1/4 CH_2Cl_2/hexane gave two orange bands, the first of which was $Re_2(CO)_5(C_4Ph_4)(DPA)$ (**4**) and the second of which contained $Re_2(CO)_4(C_6Ph_6)(DPA)$ (**3**). A third red-orange band containing an as yet unidentified organometallic compound, **5**, was eluted with 1/1 acetone/CH_2Cl_2. Chromatography of the red-orange residue from the initial photolysis with 1/4 CH_2Cl_2/hexane gave 3 bands: the first burgundy-colored band contained $Re_2(CO)_7(DPA)_2$ (**1**), and the second and third orange bands were compounds **4** and **3**. Subsequent elution with 1/1 acetone/CH_2Cl_2 gave the same organometallic compound **5** obtained above. The combined yields of **1**, **3**, and **4** based on the amount of $H_3Re_3(CO)_{12}$ used were 0.4, 4.4, and 6.5% respectively. The yield of $Re_2(CO)_{10}$ was not accurately determined but it is clearly > 25%. In a separate experiment, all volatile products and solvent were removed from the irradiated solution by vacuum distillation. An IR spectrum of the distillate clearly showed the presence of $HRe(CO)_5$ (ν(CO) 2015, 2005m, cm^{-1}; lit. [6] ν(CO) 2131.1vw, 2042.5vw,sh, 2014.5s, 2005.3m, 1982.3vw, cm^{-1}).

Irradiation of $Re_2(CO)_{10}$ with DPA

$Re_2(CO)_{10}$ (Pressure Chemical Co.) (0.19 g, 0.29 mmol) and DPA (1.03 g, 5.8 mmol) were dissolved in 30 ml dry, N_2-saturated pentane and irradiated as described above. The IR spectrum of the resultant olive-green solution showed that unreacted $Re_2(CO)_{10}$ was by far the major component. This solution was evaporated to dryness and the blue-green residue chromatographed on Kieselgel 60. Elution with 1/1 hexane/CH_2Cl_2 gave a dark blue band of an unidentified compound. Elution with 1/1 CH_2Cl_2/acetone gave two yellow bands which contained trace amounts of unidentified compounds. However, their IR spectra did not match those of any of the compounds **1**–**5**.

X-ray structure determination of $Re_2(CO)_4(C_6Ph_6)(DPA) \cdot \frac{1}{2}$ hexane (3) and $Re_2(CO)_5(C_4Ph_4)(DPA)$ (4)

Red microcrystals of **3** and orange microplatelets of **4** were obtained by slow evaporation of saturated hexane solutions. Pertinent crystal and intensity data are listed in Table 1. The program SEARCH was used to obtain 16 and 25 accurately centered reflections for **3** and **4**, respectively, which were used in the program INDEX to obtain orientation matrices for data collection and to provide cell dimensions. Details of the data collection and reduction procedures have been previously published [7]. Systematic absences $\{0k0,\ k = 2n + 1;\ h0l,\ l = 2n + 1\}$ uniquely determined the space of group of **3** as $P2_1/c$.

The structures were solved by using normal Patterson techniques and proceeded without difficulty. Empirical absorption corrections were applied to the data with the transmission coefficients and correction factors given in Table 1. In the final cycle of least squares refinement for **4**, 307 parameters were varied including the

TABLE 1

CRYSTAL AND INTENSITY DATA FOR THE X-RAY DIFFRACTION STUDY OF $Re_2(CO)_4(C_6Ph_6)(DPA)\cdot\frac{1}{2}$ HEXANE (3) AND $Re_2(CO)_5(C_4Ph_4)(DPA)$ (4)

Compound	**4**	**3**
Crystal parameters		
Crystal dimensions (mm)	0.08×0.30×0.38	0.15×0.26×0.42
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	11.277(3)	17.048(4)
b (Å)	12.301(3)	16.676(2)
c (Å)	14.851(3)	18.569(4)
α (deg)	97.37(2)	90.000
β (deg)	104.68(2)	106.70(2)
γ (deg)	104.49(2)	90.000
V (Å^3)	1889(2)	5056(3)
Z	2	4
ρ(calc.) (g cm^{-3})	1.845	1.629
Abs. coeff. (μ) (cm^{-1})	65.37	48.95
T (°C)	22(2)	22(2)
Measurement of intensity data		
Diffractometer	Enraf–Nonius CAD4	
Radiation	Mo-K_α (λ 0.71073 Å)	
Monochromator	graphite crystal	
Takeoff angle (deg.)	2.8	2.8
Scan speed (deg/min)	1–5	1–4
Scan type	$\theta/2\theta$	$\theta/2\theta$
3 std reflections measrd every n hours	$n = 2.0$	$n = 1.5$
Empirical abs. correction	0.651–0.999	0.834–0.995
Transmission coefficients	42.4–99.8%	69.6–99.1%
Anisotropic drift correction	0.952–1.082	0.998–1.095
Data limits (deg.)	$2.8 < 2\theta < 45.5$	$2.8 < 2\theta < 44.0$
Total reflections measrd	$+h \pm k \pm l$(5382)	$+h + k \pm l$(6697)
Unique data	5382	6182
Observed data ($I > 2\sigma(I)$)	4548	3568
Mean discrepancy among multiply measrd refl.	–	0.038
Fudge factor (p)	0.03	0.03
Data/parameter	14.8	9.7
R	0.031	0.078
R_w	0.041	0.074

TABLE 2

ATOMIC POSITIONAL PARAMETERS FOR $Re_2(CO)_4(C_6Ph_6)(DPA)\cdot 1/2$ Hexane (3)

Atom	x	y	z	B(Å^2)
Re(1)	0.25754(7)	0.12607(7)	0.20509(5)	6.08(3)
Re(2)	0.28466(6)	0.02178(6)	0.33143(5)	4.31(2)
O(1)	0.167(1)	0.126(1)	0.0360(9)	12.5(8)
O(2)	0.305(1)	0.300(1)	0.1908(9)	8.5(6)
O(3)	0.395(1)	0.058(1)	0.1455(9)	14.1(6)
O(4)	0.379(1)	−0.084(1)	0.2494(8)	8.1(5)
C(1)	0.198(2)	0.128(2)	0.100(1)	9.3(8)
C(2)	0.279(1)	0.225(2)	0.192(1)	7.7(8)
C(3)	0.340(2)	0.083(2)	0.168(1)	10.6(8)
C(4)	0.342(1)	−0.047(1)	0.280(1)	5.6(7)
C(1A)	0.399(2)	0.456(2)	0.322(2)	11(1)* [a]
C(2A)	0.406(3)	0.449(3)	0.413(2)	19(2)*
C(3A)	0.486(3)	0.486(3)	0.456(2)	17(2)*
C(10)	0.347(2)	0.124(1)	0.322(1)	8.9(8)
C(11)	0.436(1)	0.152(2)	0.328(1)	7.0(7)*
C(12)	0.456(1)	0.234(2)	0.337(1)	7.0(7)*
C(13)	0.531(2)	0.254(2)	0.342(1)	7.9(8)*
C(14)	0.596(2)	0.202(2)	0.342(1)	8.0(8)*
C(15)	0.580(2)	0.123(2)	0.338(2)	8.7(8)*
C(16)	0.495(2)	0.093(2)	0.330(1)	7.7(8)*
C(20)	0.313(1)	0.148(1)	0.384(1)	3.7(5)
C(21)	0.365(1)	0.159(1)	0.463(1)	3.5(5)*
C(22)	0.363(1)	0.240(1)	0.487(1)	5.1(6)*
C(23)	0.416(1)	0.254(1)	0.561(1)	5.1(6)*
C(24)	0.462(2)	0.196(2)	0.602(1)	7.7(8)*
C(25)	0.467(2)	0.119(2)	0.573(1)	7.6(8)*
C(26)	0.413(1)	0.103(1)	0.498(1)	5.6(6)*
C(30)	0.226(1)	0.139(1)	0.358(1)	3.5(5)
C(31)	0.168(1)	0.130(1)	0.406(1)	3.8(5)*
C(32)	0.102(1)	0.075(1)	0.386(1)	4.8(6)*
C(33)	0.048(1)	0.070(1)	0.427(1)	5.5(6)*
C(34)	0.048(1)	0.125(1)	0.487(1)	6.0(6)*
C(35)	0.119(1)	0.181(2)	0.509(1)	6.9(7)*
C(36)	0.172(1)	0.185(2)	0.465(1)	6.4(7)*
C(40)	0.175(1)	0.165(1)	0.277(1)	5.0(6)
C(41)	0.151(1)	0.249(1)	0.268(1)	3.4(5)*
C(42)	0.099(2)	0.280(2)	0.199(1)	7.7(8)*
C(43)	0.076(2)	0.366(2)	0.195(2)	8.7(8)*
C(44)	0.109(1)	0.418(2)	0.254(1)	6.1(6)*
C(45)	0.153(2)	0.385(2)	0.320(1)	7.2(7)*
C(46)	0.177(1)	0.302(1)	0.328(1)	5.5(6)*
C(50)	0.132(1)	0.102(1)	0.230(1)	5.1(6)
C(51)	0.044(1)	0.103(1)	0.181(1)	5.6(6)*
C(52)	0.020(2)	0.066(2)	0.110(1)	7.5(7)*
C(53)	−0.061(2)	0.070(2)	0.070(2)	11(1)*
C(54)	−0.121(2)	0.096(2)	0.100(2)	9.4(9)*
C(55)	−0.095(2)	0.137(2)	0.177(1)	8.2(8)*
C(56)	−0.012(1)	0.138(1)	0.213(1)	5.8(6)*
C(60)	0.189(1)	0.031(1)	0.240(1)	3.4(5)
C(61)	0.153(1)	−0.052(1)	0.201(1)	5.4(6)*
C(62)	0.089(1)	−0.089(2)	0.222(1)	6.2(7)*
C(63)	0.058(2)	−0.164(2)	0.188(1)	7.8(8)*
C(64)	0.094(2)	−0.193(2)	0.131(1)	8.5(8)*

TABLE 2 (continued)

Atom	x	y	z	$B(\text{Å}^2)$
C(65)	0.139(2)	−0.153(2)	0.106(1)	8.0(8)*
C(66)	0.184(1)	−0.082(1)	0.141(1)	5.9(6)*
C(70)	0.267(1)	−0.037(1)	0.421(1)	3.7(5)
C(71)	0.236(1)	−0.044(1)	0.488(1)	4.3(5)*
C(72)	0.196(1)	−0.112(1)	0.494(1)	5.6(6)*
C(73)	0.167(2)	−0.123(2)	0.560(2)	8.7(8)*
C(74)	0.185(1)	−0.067(2)	0.614(1)	6.9(7)*
C(75)	0.226(1)	0.006(1)	0.611(1)	6.5(7)*
C(76)	0.257(1)	0.016(1)	0.544(1)	5.6(6)*
C(80)	0.289(1)	−0.083(2)	0.379(1)	6.4(7)
C(81)	0.311(1)	−0.174(1)	0.380(1)	5.6(6)*
C(82)	0.284(1)	−0.212(2)	0.310(1)	6.7(7)*
C(83)	0.313(2)	−0.296(2)	0.315(1)	8.3(8)*
C(84)	0.340(2)	−0.336(2)	0.378(1)	8.4(8)*
C(85)	0.366(2)	−0.295(2)	0.448(1)	8.0(8)*
C(86)	0.350(1)	−0.211(1)	0.447(1)	5.1(6)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $4/3\,[a^{2\star}\,B_{1,1} + b^{2\star}\,B_{2,2} + c^{2\star}\,B_{3,3} + ab(\cos\gamma)^{\star}\,B_{1,2} + ac(\cos\beta)^{\star}\,B_{1,3} + bc(\cos\alpha)^{\star}\,B_{2,3}]$.

overall scale factor, positional parameters for all nonhydrogen atoms, anisotropic thermal parameters for the metal, acetylene carbon atoms and carbonyls, and isotropic thermal parameters for the phenyl carbon atoms. For **3**, 367 parameters were varied including the overall scale factor, positional parameters for all non-hydrogen atoms, anisotropic thermal parameters for the metal, carbonyl, and acetylene carbons and isotropic thermal parameters for the phenyl carbon atoms. The center of the hexane molecule between the 3rd and 4th carbon atoms was on a $\bar{1}$ position at 1/2, 1/2, 1/2, relating one half of the molecule to the other by a center of inversion.

Convergence was achieved using a non-Poisson distribution weighting scheme with fudge factors as given in Table 1. Final R factors were $R = 0.031$ and $R_w = 0.041$ for **4**, and $R = 0.078$ and $R_w = 0.074$ for **3**, defined as $R = \Sigma(\|F_o| - F_c\|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - F_c|)^2/\Sigma w(F_c)^2]^{1/2}$. In the last cycle of refinement the maximum shift per error was 0.11 for **3** and 0.01 for **4**. A final difference map showed the largest peak to be less than 0.31 times the height of a carbon atom for **3**, and 0.13 for **4**. Final positional parameters for the non-hydrogen atoms of **3** and **4** are listed in Tables 2 and 3, respectively. Selected bond distances and angles are given in Tables 4 and 5. The structure factors, general temperature factors, and complete lists of bond distances and angles are available from the author (GLG) upon request.

Results and discussion

Irradiation of $H_3Re_3(CO)_{12}$ and $Re_2(CO)_{10}$ in the presence of $PhC{\equiv}CPh$

$H_3Re_3(CO)_{12}$ does not react with diphenylacetylene when stirred at room temperature. However, rapid reaction ensues when hydrocarbon solutions of $H_3Re_3(CO)_{12}$ and DPA are irradiated with 366 nm or pyrex-filtered light. A complex mixture of products is produced with the major ones and those thus far identified shown in eq.

TABLE 3. ATOMIC POSITIONAL PARAMETERS FOR $Re_2(CO)_5(C_4Ph_4)(DPA)$ (4) (Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}\times[a^{2\star}\ B_{1,1}+b^{2\star}\ B_{2,2}+c^{2\star}\ B_{3,3}+ab(\cos\gamma)^{\star}\ B_{1,2}+ac(\cos\beta)^{\star}\ B_{1,3}+bc(\cos\alpha)^{\star}\ B_{2,3}])$

Atom	x	y	z	B (Å^2)
Re(1)	0.16109(2)	0.07219(2)	0.35285(2)	2.038(6)
Re(2)	0.21812(2)	0.31657(2)	0.36865(2)	2.142(6)
O(1)	0.3270(5)	0.1620(5)	0.5607(4)	4.1(1)
O(2)	−0.0701(5)	0.0587(5)	0.4343(4)	4.6(1)
O(3)	0.4313(5)	0.4145(5)	0.5568(4)	4.3(1)
O(4)	0.2562(6)	0.5561(5)	0.3237(4)	5.1(2)
O(5)	0.0279(5)	0.3720(6)	0.4684(4)	5.6(2)
C(1)	0.2649(6)	0.1383(6)	0.4835(5)	2.9(2)
C(2)	0.0124(7)	0.0613(6)	0.4047(5)	3.1(2)
C(3)	0.3517(7)	0.3811(6)	0.4868(5)	2.6(2)
C(4)	0.2439(7)	0.4664(7)	0.3406(5)	3.3(2)
C(5)	0.0990(7)	0.3516(7)	0.4311(5)	3.4(2)
C(10)	0.0879(7)	−0.1023(6)	0.3134(5)	2.4(2)
C(11)	−0.0083(7)	−0.2063(6)	0.3077(5)	2.8(1)*
C(12)	0.0222(7)	−0.3096(7)	0.3050(6)	3.8(2)*
C(13)	−0.0710(9)	−0.4107(8)	0.2969(7)	5.1(2)*
C(14)	−0.1949(9)	−0.4146(9)	0.2886(7)	5.5(2)*
C(15)	−0.2301(9)	−0.3137(9)	0.2882(7)	5.3(2)*
C(16)	−0.1354(8)	−0.2080(8)	0.2999(6)	4.3(2)*
C(20)	0.1926(6)	−0.0659(7)	0.2868(5)	2.8(2)
C(21)	0.2687(6)	−0.1137(6)	0.2364(5)	2.7(1)*
C(22)	0.3342(7)	−0.1876(7)	0.2732(6)	3.7(2)*
C(23)	0.4022(8)	−0.2372(8)	0.2212(7)	4.9(2)*
C(24)	0.3993(9)	−0.2145(8)	0.1318(7)	4.9(2)*
C(25)	0.3343(8)	−0.1434(8)	0.0944(6)	4.7(2)*
C(26)	0.2695(7)	−0.0885(7)	0.1475(5)	3.4(2)*
C(30)	0.3208(6)	0.1839(5)	0.3212(5)	2.3(1)
C(31)	0.4583(6)	0.1995(6)	0.3709(5)	2.4(1)*
C(32)	0.5535(6)	0.3060(6)	0.3887(5)	2.8(1)*
C(33)	0.6827(7)	0.3194(7)	0.4348(6)	3.8(2)*
C(34)	0.7192(8)	0.2266(7)	0.4637(6)	3.9(2)*
C(35)	0.6277(7)	0.1214(7)	0.4473(6)	3.8(2)*
C(36)	0.4980(7)	0.1083(6)	0.4019(5)	3.0(1)*
C(40)	0.2882(6)	0.2379(6)	0.2461(4)	2.4(2)
C(41)	0.3779(6)	0.2971(6)	0.1950(5)	2.4(1)*
C(42)	0.4460(7)	0.2312(7)	0.1578(5)	3.2(2)*
C(43)	0.5275(8)	0.2785(7)	0.1064(6)	4.0(2)*
C(44)	0.5393(8)	0.3889(8)	0.0915(6)	4.4(2)*
C(45)	0.4698(8)	0.4544(8)	0.1267(6)	4.3(2)*
C(46)	0.3898(7)	0.4075(7)	0.1788(5)	3.6(2)*
C(50)	0.1530(6)	0.2268(6)	0.2106(5)	2.4(2)
C(51)	0.0951(6)	0.2655(6)	0.1235(5)	2.5(1)*
C(52)	0.0165(7)	0.3370(7)	0.1251(6)	3.7(2)*
C(53)	−0.0405(9)	0.3707(8)	0.0421(7)	5.0(2)*
C(54)	−0.0170(9)	0.3325(9)	−0.0429(7)	5.3(2)*
C(55)	0.0576(9)	0.2605(8)	−0.0451(6)	5.0(2)*
C(56)	0.1149(7)	0.2262(7)	0.0377(6)	3.7(2)*
C(60)	0.0767(6)	0.1647(6)	0.2595(5)	2.4(2)
C(61)	−0.0658(6)	0.1247(6)	0.2204(5)	2.5(1)*
C(62)	−0.1495(7)	0.1703(7)	0.2571(6)	3.8(2)*
C(63)	−0.2822(8)	0.1179(8)	0.2187(6)	4.5(2)*
C(64)	−0.3307(9)	0.0296(8)	0.1434(7)	5.2(2)*
C(65)	−0.2510(9)	−0.0184(9)	0.1041(7)	5.5(2)*
C(66)	−0.1174(8)	0.0307(7)	0.1427(6)	4.0(2)*

1. $Re_2(CO)_{10}$ is clearly the dominant product, being formed in > 25% yield based on

$$H_3Re_3(CO)_{12} + DPA \xrightarrow{h\nu}$$

$$HRe(CO)_5 + Re_2(CO)_{10} + \underset{(\mathbf{1})}{Re_2(CO)_7(DPA)_2}$$

$$+ \underset{(\mathbf{3})}{Re_2(CO)_4(C_6Ph_6)(DPA)} + \underset{(\mathbf{4})}{Re_2(CO)_5(C_4Ph_4)(DPA)} + \mathbf{5} + \ldots \qquad (1)$$

the amount of $H_3Re_3(CO)_{12}$ employed, with compounds **1**, **3**, and **4** produced in

TABLE 4

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (deg.) FOR $Re_2(CO)_4(C_6Ph_6)(DPA)\cdot\frac{1}{2}$ Hexane (3) WITH ESTIMATED STANDARD DEVIATIONS

Bond lengths			
Re(1)–Re(2)	2.849(1)	Re(2)–C(4)	1.93(2)
Re(1)–C(1)	1.93(2)	Re(2)–C(10)	2.04(3)
Re(1)–C(2)	1.71(3)	Re(2)–C(20)	2.31(1)
Re(1)–C(3)	1.88(2)	Re(2)–C(30)	2.31(1)
Re(1)–C(10)	2.27(2)	Re(2)–C(60)	1.99(1)
Re(1)–C(40)	2.30(1)	Re(2)–C(70)	2.03(1)
Re(1)–C(50)	2.36(2)	Re(2)–C(80)	1.95(2)
Re(1)–C(60)	2.18(1)		
C(1)–O(1)	1.15(2)	C(3)–O(3)	1.20(2)
C(2)–O(2)	1.33(2)	C(4)–O(4)	1.15(2)
C(10)–C(20)	1.49(2)	C(40)–C(50)	1.42(2)
C(20)–C(30)	1.43(2)	C(50)–C(60)	1.51(2)
C(30)–C(40)	1.56(2)	C(70)–C(80)	1.22(2)
Bond angles			
Re(2)–Re(1)–C(1)	139.4(6)	Re(1)–Re(2)–C(4)	86.5(5)
Re(2)–Re(1)–C(2)	135.2(6)	Re(1)–Re(2)–C(10)	52.3(5)
Re(2)–Re(1)–C(3)	96.2(6)	Re(1)–Re(2)–C(20)	75.9(4)
Re(2)–Re(1)–C(10)	45.2(6)	Re(1)–Re(2)–C(30)	71.5(4)
Re(2)–Re(1)–C(40)	70.9(5)	Re(1)–Re(2)–C(60)	49.7(4)
Re(2)–Re(1)–C(50)	70.9(4)	Re(1)–Re(2)–C(70)	160.6(4)
Re(2)–Re(1)–C(60)	44.2(4)	Re(1)–Re(2)–C(80)	154.0(5)
Re(1)–C(1)–O(1)	175(2)	Re(1)–C(3)–O(3)	177(2)
Re(1)–C(2)–O(2)	172(2)	Re(2)–C(4)–O(4)	177(2)
Re(1)–C(10)–C(20)	115(1)	Re(1)–C(40)–C(30)	103(1)
Re(2)–C(10)–C(20)	80(1)	Re(1)–C(40)–C(50)	74.5(9)
Re(2)–C(20)–C(10)	60(1)	C(30)–C(40)–C(50)	115(1)
Re(2)–C(20)–C(30)	72.0(8)	Re(1)–C(50)–C(40)	69.9(9)
C(10)–C(20)–C(30)	108(2)	Re(1)–C(50)–C(60)	64.4(8)
Re(2)–C(30)–C(20)	72.0(8)	C(40)–C(50)–C(60)	108(2)
Re(2)–C(30)–C(40)	100.4(8)	Re(1)–C(60)–Re(2)	86.1(5)
C(20)–C(30)–C(40)	122(1)	Re(1)–C(60)–C(50)	77.1(9)
		Re(2)–C(60)–C(50)	120(1)
Re(2)–C(70)–C(80)	69(1)	Re(2)–C(80)–C(70)	69(1)
C(71)–C(70)–C(80)	137(2)	C(70)–C(80)–C(81)	136(2)

minute quantities with isolated yields of 0.4, 4.4, and 6.5% respectively. The yield of $HRe(CO)_5$ could not be determined because of its volatility but its presence was clearly inferred from its characteristic IR spectrum in the distillate from the irradiated solution. At least one other organometallic product, **5**, is formed in very low yield (< 10%) but it has not been characterized. Irradiation of $Re_2(CO)_{10}$ in presence of DPA under the same experimental conditions yields no detectable amounts of compounds **1**, **3–5** implying that $Re_2(CO)_{10}$ is not a precursor to these compounds but rather a decomposition product of $H_3Re_3(CO)_{12}$ and/or complexes **1**,**3**,**4**, and **5**.

Since $H_2Re_2(CO)_8$ is formed when $H_3Re_3(CO)_{12}$ is irradiated in the absence of DPA [1,8], we wondered whether this unsaturated dimer could be a precursor to the

TABLE 5

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (deg.) WITH ESTIMATED STANDARD DEVIATIONS FOR $Re_2(CO)_5(C_4Ph_4)(DPA)$ (**4**)

Bond lengths			
Re(1)–Re(2)	2.878(1)	Re(2)–C(3)	1.919(6)
Re(1)–C(1)	1.940(7)	Re(2)–C(4)	1.910(6)
Re(1)–C(2)	1.998(6)	Re(2)–C(5)	1.916(6)
Re(1)–C(10)	2.043(5)	Re(2)–C(30)	2.359(5)
Re(1)–C(20)	2.006(6)	Re(2)–C(40)	2.351(5)
Re(1)–C(30)	2.170(5)	Re(2)–C(50)	2.307(5)
Re(1)–C(60)	2.099(5)	Re(2)–C(60)	2.255(5)
O(1)–C(1)	1.138(7)	C(10)–C(20)	1.329(7)
O(2)–C(2)	1.120(7)	C(30)–C(40)	1.388(7)
O(3)–C(3)	1.135(7)	C(40)–C(50)	1.446(7)
O(4)–C(4)	1.144(7)	C(50)–C(60)	1.407(7)
O(5)–C(5)	1.141(7)		
Bond angles			
Re(1)–Re(2)–C(3)	105.0(2)	Re(2)–Re(1)–C(1)	74.6(2)
Re(1)–Re(2)–C(4)	163.6(2)	Re(2)–Re(1)–C(2)	93.4(2)
Re(1)–Re(2)–C(5)	102.0(2)	Re(2)–Re(1)–C(10)	166.5(2)
Re(1)–Re(2)–C(30)	47.7(1)	Re(2)–Re(1)–C(20)	141.8(2)
Re(1)–Re(2)–C(40)	70.3(1)	Re(2)–Re(1)–C(30)	53.5(1)
Re(1)–Re(2)–C(50)	70.2(1)	Re(2)–Re(1)–C(60)	51.0(2)
Re(1)–Re(2)–C(60)	46.3(1)		
Re(1)–C(30)–Re(2)	78.8(2)	Re(1)–C(60)–Re(2)	82.7(2)
Re(1)–C(1)–O(1)	170.4(5)	Re(2)–C(3)–O(3)	176.9(5)
Re(1)–C(1)–O(2)	177.9(5)	Re(2)–C(4)–O(4)	178.2(6)
		Re(2)–C(5)–O(5)	179.7(6)
Re(1)–C(10)–C(20)	69.3(3)	Re(2)–C(30)–C(40)	72.6(3)
Re(1)–C(20)–C(10)	72.4(3)	Re(2)–C(40)–C(30)	73.2(3)
Re(1)–C(30)–C(40)	115.6(4)	Re(2)–C(40)–C(50)	70.3(3)
Re(1)–C(60)–C(50)	117.5(4)	Re(2)–C(50)–C(40)	73.6(3)
C(10)–Re(1)–C(20)	38.3(2)	Re(2)–C(50)–C(60)	70.0(3)
C(30)–Re(1)–C(60)	75.4(2)	Re(2)–C(60)–C(50)	74.1(3)
C(30)–Re(2)–C(40)	34.3(2)	C(40)–Re(2)–C(50)	36.2(2)
C(30)–Re(2)–C(50)	61.6(2)	C(40)–Re(2)–C(60)	62.7(2)
C(30)–Re(2)–C(60)	68.9(2)	C(50)–Re(2)–C(60)	35.9(2)
C(11)–C(10)–C(20)	140.2(5)	C(10)–C(20)–C(21)	138.6(6)
C(30)–C(40)–C(50)	114.9(5)	C(40)–C(50)–C(60)	114.4(5)

TABLE 6

INFRARED AND MASS SPECTRAL DATA FOR COMPLEXES 1, AND 3–5

Compound	ν(CO) (cm^{-1})	M^+	Fragmentation pattern
$Re_2(CO)_7(DPA)_2$ (1)	(n-hexane)2085w, 2035s, 2015m, 1992m 1979s, 1958vw, 1948w,br	924	$M - n$CO (n = 1–7)
$Re_2(CO)_4(C_6Ph_6)(DPA)$ (3)	(n-hexane)2035vs, 1997m, 1962m, 1942w,br (CH_2Cl_2)2025s, 1990m, 1957m,br, 1932m,br	1196	$M - n$CO (n = 1–4); M – 4CO – DPA
$Re_2(CO)_5(C_4Ph_4)(DPA)$ (4)	(n-hexane)2046s, 2019s, 1967m,br 1947w,br, 1928m,br	1046	$M - n$CO (n = 1–5); M – 5CO – DPA
5 [a]	(CH_2Cl_2)2044s, 2035s, 2009m,sh, 1999vs, 1953s,br, 1912m,br, 1867w,br	[b]	–

[a] See text. [b] Not sufficiently volatile.

observed complexes, However, in separate experiments, it was shown that $H_2Re_2(CO)_8$ does not react with DPA under thermal or photochemical conditions [1] and thus it cannot be a precursor to these products.

The HRe(CO)$_5$ and $Re_2(CO)_{10}$ products were identified by comparison of their IR spectra to authentic samples. IR and mass spectral data for compounds **1**, **3**, and **4** are summarized in Table 6 along with IR data for **5**. Complexes **1** and **3** are apparently the same compounds that were isolated by Mays et al. [2] from the thermal reaction of $Re_2(CO)_{10}$ with DPA. These were spectroscopically characterized by Mays et al. [2], and our data are essentially identical. We have further characterized **3** by a complete single crystal X-ray diffraction study, details of which are given below. Compound **4** was not mentioned by Mays et al., although its yield is the highest of all the DPA containing products observed in this study. This compound has also been structurally characterized (see below). Compounds **1** and **4** are apparently the same as the two compounds which we originally [1] formulated as $H_2Re_2(CO)_7(DPA)_2$ and $H_2Re_2(CO)_5(DPA)_3$, but the present study and that of Mays et al. [2] show these formulations to be incorrect as they do not have hydride ligands. The absence of hydride ligands is indicated by the absence of ^1H NMR signals in the metal hydride region for these compounds.

Crystal and molecular structures of $Re_2(CO)_4(C_6Ph_6)(DPA) \cdot \frac{1}{2}$ hexane (3) and $Re_2(CO)_5(C_4Ph_4)(DPA)$ (4)

ORTEP drawings showing the molecular structures of **3** and **4** are given in Fig. 1 and 2. Relevant bond lengths and angles are listed in Tables 4 and 5. Compound **4** has two DPA molecules linked together in a rhenacyclopentadiene ring. This structural unit is the first reported for rhenium but is otherwise typical of metallacyclopentadienes found in other complexes [3]. In **4**, this ring is bound in a π-fashion to the other rhenium atom (Re(2)), much like the structures of $Fe_2(C_4R_4)(CO)_6$ [9] and $Cr_2(CO)(\eta\text{-}C_5H_5)_2(C_4Ph_4)$ [4d]. The maximum deviation from the least-squares plane defined by Re(1), C(30), C(40), C(50), and C(60) is 0.13 Å for C(60). The rhenium atom within the metallacycle (Re(1)) is also ligated by an η^2-DPA and two carbonyls, while Re(2) has three carbonyl ligands. The Re–Re distance in **4** (2.878(1) Å) is less than the intermetallic distance in $Re_2(CO)_{10}$ (3.02 Å) [10] but the effect of the bridging ligand on the rhenium–rhenium distance is not known.

The structural features of the η^2-DPA ligand in **4** are of particular interest since this is the first structurally characterized Re alkyne complex. A central question that arises is whether the η^2-DPA ligand acts as a formal 2- or 4-electron donor to Re(1). To satisfy the 18 electron rule at each Re center, the molecule must have either a Re=Re double bond and a 2-electron donor DPA or a Re–Re single bond and a 4-electron donor DPA. Recent work has shown that the most reliable indications of 2- vs. 4-electron alkyne ligands are the ^{13}C NMR chemical shifts of the alkyne carbons [11] and the metal–alkyne carbon bond distances [12]. The low yields of complexes **3** and **4** have precluded measurement of their ^{13}C NMR spectra. The

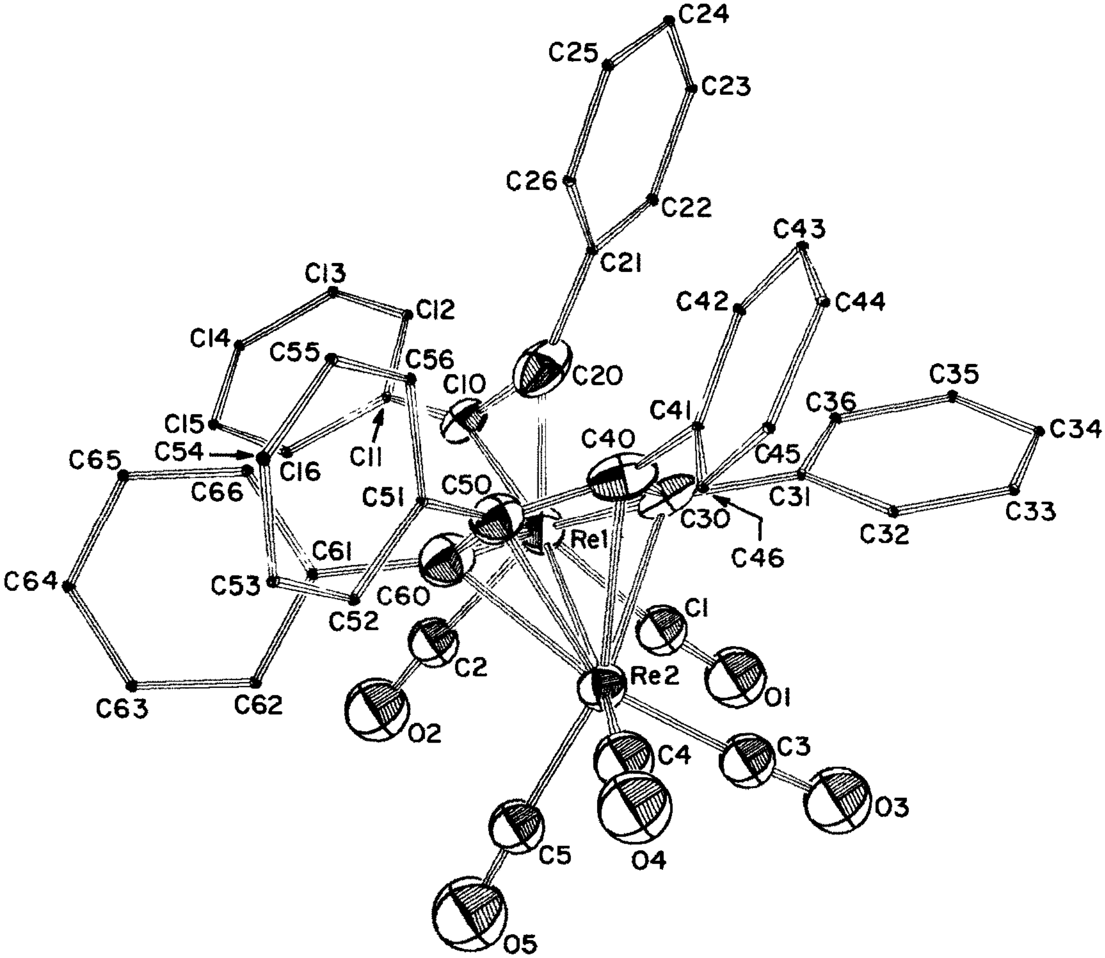


Fig. 1. ORTEP drawing of $Re_2(CO)_4(C_6Ph_6)(DPA)\cdot\frac{1}{2}$ Hexane (3). The thermal ellipsoids are drawn at the 50% probability level. For clarity, only the phenyl carbons attached to the bridging C_6Ph_6 ligand are drawn.

bond distance criteria require comparisons to be made to established metal-carbon distances in metal-alkyne complexes in which the question of 2- or 4-electron donation is unambiguous. Since the structures described here are the first which possess η^2-alkynerhenium groups, an appropriate comparison cannot be made. However, alkynetungsten complexes which have a demonstrated 4-electron alkyne ligand show an average W–alkyne-carbon distance of 2.04(3) Å [13]. This is 0.10 Å longer than the average W=C double bond length (1.94(6) Å) based on the three neopentylidene complexes reported by Churchill et al. [14]. If the η^2-DPA ligand in **4** acts as a four-electron donor, we expect a comparable elongation of the Re=C bond in going from a typical carbene Re=C double bond to the Re–C distance in the alkyne complexes. The two Re carbene complexes $[(\eta\text{-}C_5Me_5)Re(NO)(P(OPh)_3)(=CH_2)]PF_6$ [15] and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]PF_6$ [16] have Re=C dis-

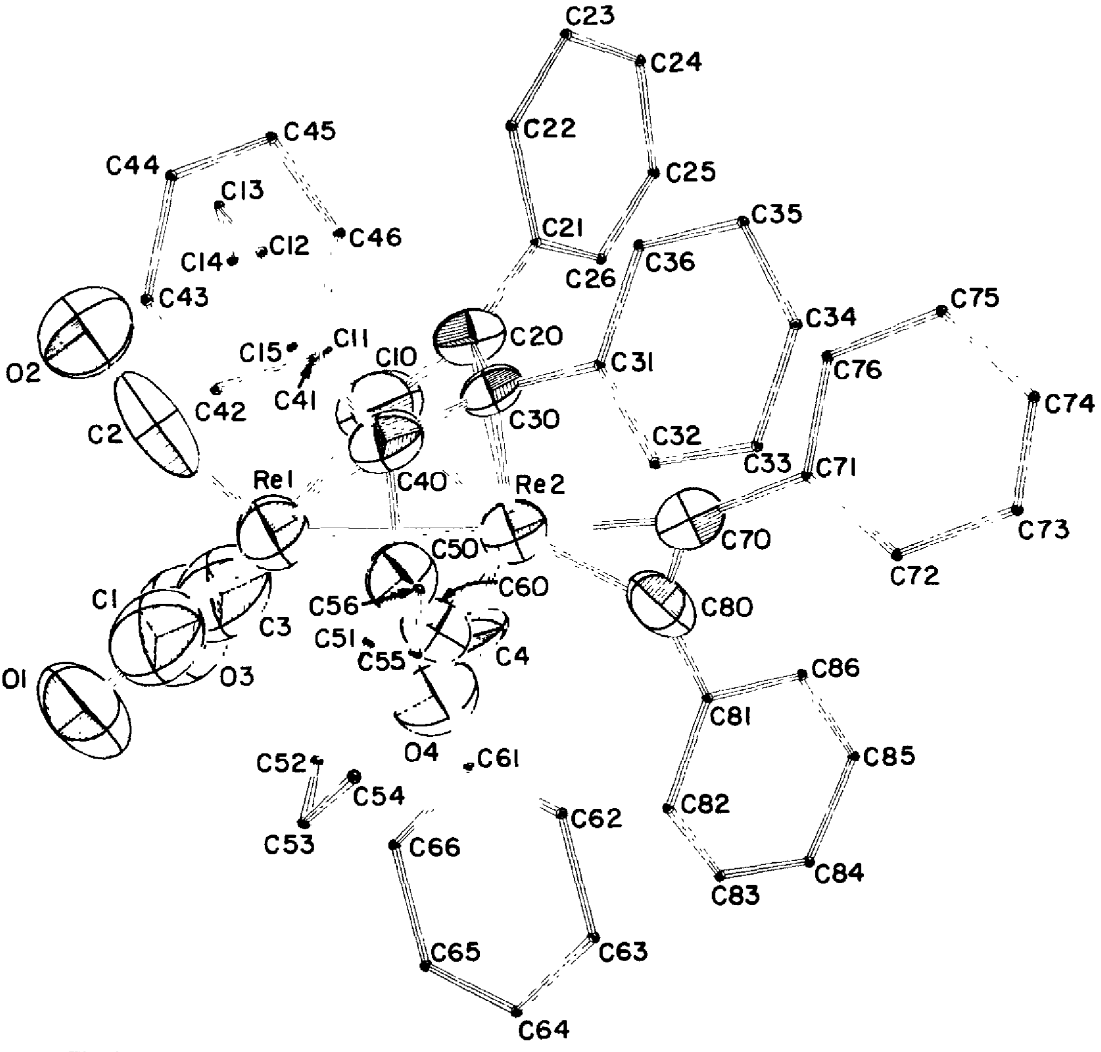


Fig. 2. ORTEP drawing of $Re_2(CO)_5(C_4Ph_4)(DPA)$ (4). The thermal ellipsoids are drawn at the 50% probability level. For clarity, only the phenyl carbons attached to the rhenacyclopentadiene ring are drawn.

tances of 1.898(18) and 1.949(6) Å, respectively. A rhenium carbon distance of 2.02(4) Å should thus be expected if the alkyne ligand in **4** functioned as a four-electron donor. Indeed, the Re(1)–alkyne carbon bond distances in **4** are 2.043(5) and 2.006(6) Å, implying that the alkyne is a 4-electron donor ligand in **4**. Consistent with this conclusion is the observation that the orientation of the alkyne ligand in **4** is such that the C≡C bond is virtually co-planar with carbonyl C(2)–O(2), having a C(10)–C(20)–Re(1)–C(2) torsional angle of 0.6°. Such an orientation has been shown to be preferred for 4-electron alkynes [17].

Another factor which indicates that the η^2-DPA ligand in **4** acts as a 4-e^- donor is Mays et al. [2] proposed rhenacyclopentadiene structure for compound **1**. The only difference between **1** and **4** is that a DPA ligand in **4** has replaced two carbonyl ligands in **1**, implying that the electronic contribution of the DPA is equivalent to that of two carbonyls, i.e., a four electron donor.

In $Re_2(CO)_4(C_6Ph_6)(DPA)$ (**3**), three of the alkynes have linked together in what is often called a "fly-over bridge", a structural feature now structurally demonstrated for four other complexes [2,4a-c] and proposed for six others [4d,e]. The geometry of this bridging system in **3** is typical of that in the other compounds and deserves little comment. The end carbons C(10) and C(60) are bonded to both Re atoms, although each lies slightly closer to Re(2) (Table 4). Each is further incorporated into an η^3-allyl ligand which is π-bonded to just one rhenium. The entire C_6Ph_6 ligand thus serves as a total eight electron donor to the binuclear complex. One of the rhenium atoms (Re(1)) is bound to three carbonyl ligands while the other (Re(2)) has one carbonyl and an η^2-DPA ligand. The Re–Re distance of 2.849(1) in **3** is slightly shorter than in **4**. However, this interatomic distance is much longer than in the triply-bonded dimer $Re_2(\eta\text{-}C_3H_5)_4$ (2.225(7) Å [18], or even in the related complex $Re_2(CO)_4(C_6Ph_6)(CNR)_2$ reported by Mays et al. [2] (Re–Re 2.786(1) Å).

As in compound **4** the question of 2 vs. 4-e^- donation of the η^2-DPA ligand arises. To satisfy the 18 valence electron rule, complex **3** must have either a Re=Re double bond and a 2-e^- DPA or a Re–Re single bond and a 4-e^- DPA ligand. The Re-alkyne carbon bond distances in **3** are 2.03(1), and 1.95(2) Å, and as discussed above these imply a 4e^- ligand as also does the observation of near co-planarity of the alkyne C≡C bond and carbonyl C(4)–O(4) (C(70)–C(80)–Re(2)–C(4) torsional angle 13.0°). Additional evidence supporting the 4-electron donor role of the η^2-DPA ligand is the fact that **4** and Mays et al.'s [2] compound $Re_2(CO)_4(C_6Ph_6)(CNR)_2$ (**6**), have similar structures except that the DPA ligand in **4** has replaced the two CNR ligands of **6**.

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