Contribution from the Department of Chemistry,
Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Bimetallic Aryldiazenido Complexes. Crystal and Molecular Structure of $(\eta\text{-}C_5H_5)(CO)(p\text{-}N_2C_6H_4OMe)ReAuPPh_3$

CARLOS F. BARRIENTOS-PENNA, FREDERICK W. B. EINSTEIN, TERRY JONES, and DEREK SUTTON*

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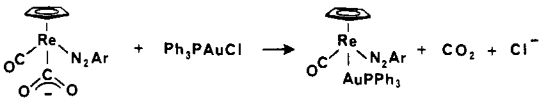
$(\eta\text{-}C_5H_5)(CO)(p\text{-}N_2C_6H_4OMe)ReAuPPh_3$ (compound **2**) has been synthesized from the reaction of the lithium salt of the rhenium carboxylate complex anion $[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(CO_2)]^-$ (**1**) with Ph_3PAuCl in CH_2Cl_2. It crystallizes in the space group $P2_1/n$ with a = 10.960 (2) Å, b = 14.313 (6) Å, c = 18.856 (5) Å, β = 101.13 (2)°, V = 2902.4 Å^3, and Z = 4. The calculated and measured densities are 2.00 and 1.98 (1) g cm^{-3} respectively. On the basis of 2319 observed X-ray-counter-measured intensities with $I \geq 3\sigma(I)$ in the range 45° ≥ 2θ (MoKα), the structure was solved and refined by full-matrix least-squares methods to R = 0.039 and R_w = 0.045. Important bond lengths and angles are Re-Au = 2.615 (1) Å, Re-N = 1.78 (2) Å, N-N = 1.27 (2) Å, Re-Au-P = 175.3 (1)°, and Re-N(1)-N(2) = 171 (1)°. The synthetic method exploits the facile decarboxylation of the anion in **1** in the formation of the Re-Au bond in **2**.

Introduction

In a preceding paper[1] we have described the isolation and characterization of the rhenium carboxylate anionic complex $[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(CO_2)]^-$ (**1**), and its $(\eta\text{-}C_5Me_5)$ analogue, as the lithium or calcium salts. So far, we have been unable to grow crystals of these salts suitable for an X-ray structure analysis, which is required to define unambiguously the manner in which the CO_2 moiety is bound to the metal in this complex. Further work is continuing with this objective. Adopting an alternative strategy, we have attempted to coordinate the CO_2 moiety via either one or both of its oxygen atoms to a second transition-metal center in a crystalline complex. A limitation to this idea is the possibility that the carboxylate anion (**1**) in its reactions will undergo decarboxylation. This already is known to occur in the presence of a source of protons in organic solvents to furnish the hydride $(\eta\text{-}C_5H_5)ReH(CO)(p\text{-}N_2C_6H_4OMe)$.[1]

In this paper we describe the product of one such attempt involving the reaction of the lithium salt of **1** with Ph_3PAuCl.



1 **2** (1)

Decarboxylation has indeed taken place (eq 1), to furnish a rhenium-gold bond in the new bimetallic complex $(\eta\text{-}C_5H_5)(CO)(p\text{-}N_2C_6H_4OMe)ReAuPPh_3$ (**2**), the X-ray structure of which has been determined.

Experimental Section

Reactions and manipulations were routinely carried out in Schlenk apparatus under nitrogen. Solvents were dried by standard methods and distilled. Infrared spectra were recorded with a Perkin-Elmer Model 983 instrument, and 70-eV electron-impact mass spectra were obtained by G. Owen using a Hewlett-Packard Model 5985 instrument. Elemental analysis was done by the SFU Microanalytical Laboratory (M. K. Yang); NMR spectra were measured at 400 MHz on a Bruker WM-400 spectrometer.

Preparation of $(\eta\text{-}C_5H_5)(CO)(p\text{-}N_2C_6H_4OMe)ReAuPPh_3$ (2). To a solution of $Li[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(CO_2)]$[1] (50 mg) in CH_2Cl_2 (10 mL) was added a stoichiometric amount of solid Ph_3PAuCl (53 mg), and the mixture was stirred at room temperature overnight. The color of the solution changed from yellow to orange-brown. The solution was filtered to remove LiCl, and hexane was added to precipitate the product as an air-stable orange microcrystalline solid in about 40% yield: mp 142-143 °C (dec); satisfactory C,H,N analysis obtained. IR (cm^{-1}): 1886 vs (ν(CO)), 1611 vs (ν(NN)) (CH_2Cl_2); 1885 vs, 1611 vs (acetone); 1878 vs, 1612 vs (evaporated CH_2Cl_2 solution on AgCl windows). The 70-eV electron-impact mass spectrum had no peaks corresponding to the molecular ion (m/z 874 (^{187}Re)) but was dominated by a cluster at m/z 804 (^{187}Re), which had the correct pattern of isotopic intensities for $(M - C_2H_2N_2O)^+$. ^{1}H NMR (acetone-d_6): δ 3.67 s (3 H, OMe), 5.61 s (5 H, C_5H_5), 7.55-7.63 m (19 H, PPh_3 and C_6H_4).

X-ray Structure Determination for $(\eta\text{-}C_5H_5)(CO)(p\text{-}N_2C_6H_4OMe)ReAuPPh_3$. A suitable crystal for data collection was grown from acetone-hexane and mounted in a thin-walled glass tube on an Enraf-Nonius CAD4-F diffractometer in a nonspecific orientation. An accurate unit cell was determined by least squares from the setting angles of 25 accurately centered reflections (with 17° < 2θ < 24°) chosen from a variety of points in reciprocal space and measured with Mo Kα_1 radiation (λ = 0.709 30 Å). The space group was determined as $P2_1/n$ from a "fast data collection" over a limited 2θ range (≤15°) and subsequently confirmed during structure solution and refinement. A total of 3782 independent reflections were measured, of which 2319 were classed as observed [$I/\sigma(I) \geq 3$] and used in structure solution and refinement. Lorentz, polarization, and semiempirical absorption[2] corrections have been applied. Pertinent crystallographic data are listed in Table I. The structure was

Table I. Crystallographic Data[a]

formula	$C_{31}H_{27}AuN_2O_2PRe$
fw	873.69
cryst system	monoclinic
space group[b]	$P2_1/n$
a, Å	10.960 (2)
b, Å	14.313 (6)
c, Å	18.856 (5)
β, deg	101.13 (2)
V, Å^3	2902.41
Z	4
D_{calcd}, g cm^{-3}	2.00
D_{obsd}, g cm^{-3} [c]	1.98 (1)
cryst dimens, mm	0.17 × 0.10 × 0.18
μ(Mo Kα), cm^{-1}	93.42
transmission factors[d]	0.537-0.993
scan type	ω-2θ
ω-scan speed, deg min^{-1}	0.9-2.0
scan range, deg in ω[e]	0.7 + 0.35 tan θ
data colled	$\pm h,k,l$
$2\theta_{max}$, deg	45.00
cryst decay	negligible
unique reflcns	3782
obsd reflcns	2319
no. of variables	223
R	0.039
R_w	0.045

[a] Temperature 20 ± 1 °C; Mo Kα radiation, graphite monochromator, λ = 0.709 30 Å (α_1), 0.713 59 Å (α_2); function minimized $\Sigma w(|F_o| - |F_c|)^2$, $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $R_w = (\Sigma w(|F_o| - |F_c|)^2)^{1/2}$, $w = 1/(\sigma^2(F) + 0.0006F^2)$. [b] Nonstandard setting of $P2_1/c$; equivalent positions $\pm(x, y, z; x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$. [c] Measured by flotation in CH_2Cl_2-CH_2I_2. [d] These values were determined experimentally by using a semiempirical absorption correction.[2] [e] The scan range was extended 25% on each side for background measurement.

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[2] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351.

0020-1669/85/1324-0632$01.50/0

Table II. Final Positional and Thermal Parameters for Compound **2**[a]

atom	*x*	*y*	*z*	*B*(iso), Å^2
Au(1)	0.07066 (6)	0.22368 (5)	0.97607 (4)	3.12 (3)
Re(1)	−0.02287 (6)	0.17817 (5)	0.08884 (4)	2.75 (3)
P(1)	0.1659 (4)	0.2561 (3)	0.8821 (3)	3.3 (2)
O(44)	0.283 (1)	0.667 (1)	0.112 (1)	6.0 (10)
O(6)	0.212 (1)	0.060 (1)	0.119 (1)	6.2 (9)
N(1)	0.039 (1)	0.275 (1)	0.143 (1)	3.2 (7)
N(2)	0.072 (1)	0.341 (1)	0.189 (1)	3.4 (8)
C(11)	0.293 (1)	0.176 (1)	0.881 (1)	2.8 (3)
C(12)	0.373 (2)	0.159 (1)	0.945 (1)	4.1 (4)
C(13)	0.476 (2)	0.101 (1)	0.949 (1)	4.6 (4)
C(14)	0.496 (2)	0.057 (1)	0.888 (1)	4.2 (4)
C(15)	0.416 (2)	0.073 (1)	0.824 (1)	4.0 (4)
C(16)	0.317 (1)	0.133 (1)	0.819 (1)	3.5 (3)
C(21)	0.068 (1)	0.244 (1)	0.793 (1)	2.8 (3)
C(22)	−0.009 (2)	0.165 (1)	0.780 (1)	4.4 (4)
C(23)	−0.085 (2)	0.150 (1)	0.714 (1)	5.5 (5)
C(24)	−0.089 (2)	0.217 (1)	0.661 (1)	5.3 (4)
C(25)	−0.017 (2)	0.293 (1)	0.671 (1)	5.0 (4)
C(26)	0.064 (2)	0.306 (1)	0.737 (1)	4.1 (4)
C(31)	0.235 (1)	0.373 (1)	0.880 (1)	2.9 (3)
C(32)	0.168 (1)	0.453 (1)	0.888 (1)	3.6 (4)
C(33)	0.217 (2)	0.540 (1)	0.887 (1)	4.0 (4)
C(34)	0.335 (2)	0.550 (1)	0.879 (1)	5.4 (5)
C(35)	0.406 (2)	0.471 (2)	0.871 (1)	8.7 (7)
C(36)	0.355 (2)	0.382 (2)	0.868 (1)	7.1 (6)
C(41)	0.113 (1)	0.424 (1)	0.165 (1)	3.1 (3)
C(42)	0.131 (1)	0.440 (1)	0.094 (1)	3.4 (4)
C(43)	0.184 (2)	0.524 (1)	0.079 (1)	4.6 (4)
C(44)	0.228 (2)	0.592 (1)	0.131 (1)	4.4 (4)
C(45)	0.209 (1)	0.575 (1)	0.200 (1)	3.2 (3)
C(46)	0.156 (1)	0.490 (1)	0.217 (1)	3.4 (3)
C(47)	0.332 (2)	0.736 (1)	0.167 (1)	5.2 (13)
C(51)	0.774 (2)	0.200 (1)	0.033 (1)	4.5 (13)
C(52)	0.779 (2)	0.174 (1)	0.105 (1)	5.4 (14)
C(53)	0.828 (2)	0.084 (1)	0.116 (1)	5.3 (12)
C(54)	0.850 (2)	0.053 (1)	0.048 (1)	4.7 (13)
C(55)	0.814 (1)	0.124 (2)	0.000 (1)	4.6 (13)
C(6)	0.123 (2)	0.109 (1)	0.109 (1)	3.6 (11)

[a] Esd's refer to last digit printed.

solved by conventional Fourier methods. Hydrogen atoms were fixed in their calculated positions [d(C–H) = 0.95 Å; B_{iso}(H) = 7.11 Å^2]. Methyl hydrogens were not located. Final cycles of full-matrix least-squares refinement, with selected non-hydrogen atoms refined anisotropically and hydrogen atoms included as fixed contributions, gave final agreement factors of R = 0.039 and R_w = 0.045 for 223 variables. The largest shift:error ratio during the final cycle was 0.01. The only features in the final electron density difference map were a number of peaks and troughs (±1.3 (2) e Å^{-3}) in the vicinity of the Re and Au heavy atoms. Atomic scattering factors, including anomalous dispersion, were taken from ref 3. Final positional and thermal parameters for non-hydrogen atoms are given in Table II. Anisotropic thermal parameters, hydrogen parameters, and structure factor listings have been deposited as supplemental material. All calculations were performed on an "in-house" VAX 11-750 computer using the NRC VAX Crystal Structure System set of programs.[4]

Results and Discussion

Heterobimetallic compounds with rhenium–gold bonds seem to be rather rare. An examination of the excellent compilation of bimetallic compounds given in ref 5 revealed only (CO)$_5$ReAuPPh$_3$, synthesized by Bower and Stiddard in 1968,[6] and a reference to unpublished work by Stone on Re$_2$AuH(CO)$_9$PPh$_3$. No additional compounds were found in a search of the more recent literature. Since neither of the above appears to have been studied crystallographically,[7] the X-ray structure described here for compound **2** is (surprisingly, to us) the first for a Re–Au bond.

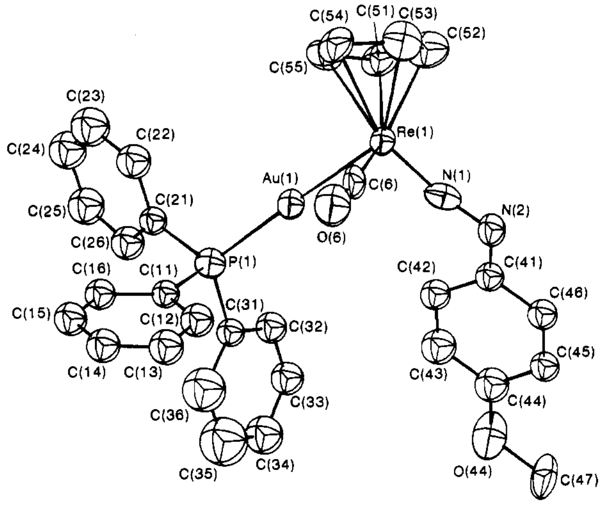

Figure 1. Perspective view of a molecule of (η-C$_5$H$_5$)(CO)(p-N$_2$C$_6$H$_4$OMe)ReAuPPh$_3$ (**2**).

Table III. Selected Bond Parameters for (η-C$_5$H$_5$)(CO)(p-N$_2$C$_6$H$_4$OMe)ReAuPPh$_3$

	Distances (Å)		
Au(1)–Re(1)	2.615 (1)	C(6)–O(6)	1.19 (2)
Au(1)–P(1)	2.271 (4)	N(1)–N(2)	1.27 (2)
Re(1)–N(1)	1.78 (2)	N(2)–C(41)	1.38 (2)
Re(1)–C(51)	2.29 (2)	C(41)–C(42)	1.41 (2)
Re(1)–C(52)	2.25 (2)	C(42)–C(43)	1.39 (3)
Re(1)–C(53)	2.25 (2)	C(43)–C(44)	1.40 (3)
Re(1)–C(54)	2.31 (2)	C(44)–C(45)	1.39 (3)
Re(1)–C(55)	2.34 (2)	C(45)–C(46)	1.40 (2)
Re(1)–C(6)	1.86 (2)	C(46)–C(41)	1.39 (2)
Re(1)–CR[a]	1.96	C(44)–O(44)	1.31 (2)
P(1)–C(11)	1.81 (2)	O(44)–C(47)	1.45 (2)
P(1)–C(21)	1.82 (2)		
P(1)–C(31)	1.84 (2)		
av C–C(triphenyl)	1.38 (2)	av C–C(cyclopentadienyl)	1.39 (2)
	Angles (deg)		
Re(1)–Au(1)–P(1)	175.3 (1)	N(1)–N(2)–C(41)	119 (1)
Re(1)–C(6)–O(6)	175 (1)	N(2)–C(41)–C(42)	125 (2)
Re(1)–N(1)–N(2)	171 (1)	N(2)–C(41)–C(46)	116 (1)
		C(42)–C(41)–C(46)	118 (2)
Au(1)–Re(1)–N(1)	96.4 (4)	C(41)–C(42)–C(43)	119 (2)
Au(1)–Re(1)–C(6)	81.1 (5)	C(42)–C(43)–C(44)	124 (2)
Au(1)–Re(1)–CR[a]	111.3	C(44)–C(45)–C(46)	121 (2)
N(1)–Re(1)–C(6)	94.7 (6)	C(45)–C(46)–C(44)	122 (2)
N(1)–Re(1)–CR[a]	133.0	O(44)–C(44)–C(43)	120 (2)
C(6)–Re(1)–CR[a]	125.7	O(44)–C(44)–C(45)	124 (2)
		C(44)–O(44)–C(47)	120 (1)
av C–C–C(triphenyl)	120 (2)	av C–C–C(cyclopentadienyl)	108 (2)

[a] CR denotes the centroid of the cyclopentadienyl ring.

The structure consists of discrete *R* and *S* enantiomers of (η-C$_5$H$_5$)(CO)(p-N$_2$C$_6$H$_4$OMe)ReAuPPh$_3$, crystallographically related in the centrosymmetric space group $P2_1/n$. The structure of one enantiomer is illustrated in Figure 1, which also shows the numbering scheme. Compound **2** is a member of a class of neutral compounds of the general type (η-C$_5$H$_5$)Re(CO)(X)(N$_2$Ar) (Ar = aryl) that we have synthesized with X = H, halide, CO$_2$H, OCHO, NCO, CO$_2$Me, and CONMe$_2$ among others.[1,8] Here X is AuPPh$_3$, and the existence of compound **2** might be anticipated from the isolobal relationship of H with AuPPh$_3$.[9] Several

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examples have been described recently in which the AuPPh$_3$ ligand occupies the role of a hydride in a related compound.[10] As expected, the Re–Au–P group in **2** is nearly linear (Re–Au–P = 175.3°). The Re–Au bond length is 2.615 Å. Other metrical details of the structure (Table III) are unexceptional. The (*p*-methoxyphenyl)diazenide ligand adopts the singly bent structure expected to be present from the ν(NN) value of ca. 1612 cm^{-1} and has reasonable values for Re–N (1.78 Å), N–N (1.27 Å), Re–N–N (171°), and N–N–C(aryl) (119°).

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Registry No. **1** (Ar = C$_6$H$_4$-*p*-OMe), 94518-43-1; **2** (Ar = C$_6$H$_4$-*p*-OMe), 94518-44-2; Ph$_3$PAuCl, 14243-64-2.

Supplementary Material Available: Anisotropic thermal parameters (Table S1), calculated positional and thermal parameters for hydrogen atoms (Table S2), additional bond parameters (Table S3), and the observed and calculated structure amplitudes (Table S4) (21 pages). Ordering information is given on any current masthead page.

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Notes

Contribution from the P. M. Gross Chemical Laboratory,
Duke University, Durham, North Carolina 27706

Crown Ether–Lanthanide Complexes Studied by CPL and TL. 1. Solution Stoichiometry of Europium and Terbium Nitrate Complexes of (2*R*,3*R*,11*R*,12*R*)-2,3,11,12-Tetramethyl-18-crown-6

D. H. Metcalf, R. G. Ghirardelli, and R. A. Palmer*

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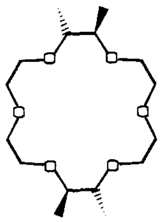
Although numerous papers describing the syntheses and solid-state structures of crown ether complexes of lanthanide salts have appeared recently,[1] there are few reports of solution studies. Izatt and co-workers determined formation constants for 18-crown-6 complexes of lanthanide chlorides in methanol by calorimetry,[2] Bünzli and Wessner used ^{1}H NMR to find formation constants of lanthanide nitrate–15-crown-5 and –18-crown-6 complexes in acetonitrile,[3] and more recently, Massaux and co-workers described a competitive potentiometric technique for determining the formation constants of lanthanide complexes of several crowns and crown derivatives in propylene carbonate.[4] Other papers have reported the limited success of the use of the ^{1}H NMR shifting properties of paramagnetic lanthanides to determine the solution structure of crown complexes.[5,6] As part of an extensive study of the use of circularly polarized luminescence (CPL) and total luminescence (TL) in probing crown ether–lanthanide interactions in nonaqueous solvents, we describe here the results of an anion-exchange experiment designed to elucidate the solution stoichiometry of a chiral crown ether–lanthanide nitrate complex in trifluoroethanol (TFE).

The CPL experiment measures the differential emission of left and right circularly polarized light by a chiral luminophore when it is excited with unpolarized light.[7] CPL is sensitive to solution structure when a (achiral) luminophore gains chirality through association with a chiral ligand. For lanthanides, CPL is much more easily measured than CD because of the inherent sensitivity of emission measurements and the weakness of f–f transitions in absorption. Although all lanthanides are capable of exhibiting CPL in chiral crystals, only europium(III) and terbium(III) exhibit significant luminescence in solution, and thus solution CPL studies of lanthanides are normally limited to these ions.[8] The more useful CPL-active transitions are the $^7F_2$, $^7F_1 \leftarrow {}^5D_0$ transitions of europium(III) at ca. 618 and 595 nm, respectively, and the $^7F_5 \leftarrow {}^5D_4$ transition of terbium(III) at ca. 545 nm. CPL studies of europium(III) and terbium(III) complexes of various chiral ligands have appeared in the recent literature.[9]

In the case of europium(III) the total luminescence also can be very useful for solution studies. First, since the $^7F_0 \leftarrow {}^5D_0$ transition, at ca. 578 nm, cannot exhibit more than a single line regardless of ligand field, any apparent splitting of this transition is clear evidence of the presence of more than one europium(III) species. Second, the TL of the $^7F_1 \leftarrow {}^5D_0$ transition is predominantly magnetic dipole allowed, and so its intensity is relatively unaffected by the europium environment. However, the crystal field splitting of this transition does give limited information on the symmetry about the lanthanide. In nonaxial ligand fields, i.e., those with lower than threefold axes, three components are expected for this transition. Finally, the $^7F_2 \leftarrow {}^5D_0$ transition is *hypersensitive*, and its intensity can be related to the polarizability of the attached ligands.[10,11] Unfortunately, the TL bands of terbium(III) are more complex and do not lend themselves to such fruitful interpretation.

Our experiments consisted of measuring the CPL and TL spectra of 0.06 M TFE solutions of (2*R*,3*R*,11*R*,12*R*)-2,3,11,12-tetramethyl-18-crown-6 (I) and either europium(III) or terbium(III) perchlorate in a 1:1 crown ether:lanthanide ratio, during the course of a titration with 0.55 M tetraethylammonium nitrate. The details of the synthesis of the crown ether as well as the description of the CPL instrument appear elsewhere.[12] The compounds used in these experiments were dried by using standard techniques, and care was taken to exclude water during the course of the titrations.



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