

was noticed. Eventually the reflections became too broad to be measured. When the crystal was allowed to warm up, the reflection profiles narrowed again but showed about 10% loss of intensity. The process could be repeated through several cycles with less intensity loss each time.

Re(II) shows a roughly octahedral coordination geometry with dimensions very similar to those of $[\text{Ru}(\text{bpy})_3]^{2+}$ (Figure 1; $d(\text{Ru}-\text{N}) = 2.06 \text{ \AA}$). There are only four other mononuclear octahedral Re(II) complexes available for comparison: $[\text{Re}^{\text{II}}(\text{NO})\text{Br}_4(\text{CH}_2\text{CH}_2\text{O})][\text{N}(\text{CH}_2\text{CH}_3)_4]^{16}$ (2), $[\text{Re}^{\text{II}}(\text{NO})\text{Cl}_4(\text{C}_5\text{H}_5\text{-N})][\text{N}(\text{CH}_2\text{CH}_3)_4]^{17}$ (3), $[\text{Re}^{\text{II}}(\text{NO})\text{Br}_4(\text{CH}_3\text{CN})][\text{N}(\text{CH}_2\text{C}-\text{H}_3)_4]^{16}$ (4), and $[\text{Re}^{\text{II}}(\text{CNC}(\text{CH}_3)_2(\text{CH}_3\text{CCN}))][\text{N}(\text{CH}_2\text{C}-\text{H}_3)_4]^{16}$ (4), and $[\text{Re}^{\text{II}}(\text{CNC}(\text{CH}_3)_2(\text{CH}_3\text{CN}))_2(\text{P}(\text{C}_6\text{H}_5)_3)_2](\text{B}-\text{F}_4)^{18}$ (5). The Re-NO distances in 2-4 are 1.72, 1.75, and 1.77 Å, respectively. The Re-N (pyridine) distance in 3 is 2.22 Å and the Re-NCCH₃ distance in 4 is 2.14 Å, both of which are trans to an NO ligand. In 5 the trans Re-NCCH₃ distances are 2.055 and 2.058 Å, which compare very well with the observed Re-N distance of 2.09 Å in 1. Re-N distances of three octahedral Re(V) and one octahedral Re(I) compounds with ethylenediamine, bpy, and pyridine as ligands are all about 2.15 Å.¹⁹ The observed Re2-O1 and Re2-O2 distances are 1.67 and 1.61 Å, respectively, both shorter than the 1.72 Å observed for KReO_4 .²⁰ The shortening is probably due to disorder.

Acknowledgment. A.G. is grateful to the Swiss National Science Foundation for a postdoctoral fellowship.

Supplementary Material Available: Listings of displacement parameters, bond lengths and angles, and magnetic data and a figure depicting the UV-vis spectrum for 1 (3 pages); a listing of structure factors for 1 (5 pages). Ordering information is given on any current masthead page.

- (16) Ciani, G.; Giusto, D.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1975**, 2156.
 (17) Ciani, G.; Giusto, D.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1978**, 798.
 (18) Allison, J. D.; Fanwick, P. E.; Walton, R. A. *Organometallics* **1984**, *3*, 1515.
 (19) (a) $[\text{Re}^{\text{V}}\text{Cl}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})(\text{C}_5\text{H}_5\text{N})_2]$: Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1977**, *55*, 333. (b) $[\text{Re}^{\text{V}}(\text{C}_5\text{H}_5\text{N})_4\text{O}_2]\text{Cl}$ and $[\text{Re}^{\text{V}}(\text{C}_2\text{H}_4\text{N}_2)_2\text{O}_2]\text{Cl}$: Lock, C. J. L.; Turner, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 923.
 (20) Krebs, B.; Hasse, K.-D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 1334.

Contribution from the Laboratoire de Chimie Moléculaire,
 Unité Associée au CNRS, Université de Nice,
 Parc Valrose, 06034 Nice, France

Study of the Reactivity of the Single-Chloro-Bridged Dissymmetric Dinuclear Rhodium Species

$(\text{CO})_2(\text{Cl})\text{Rh}(\mu\text{-Cl})\text{Rh}(\text{CO})[\text{PhP}(\text{OC}(\text{CH}_3)_2\text{CH}_2)_2\text{NH}]$

Pierre Brun, Pierre Vierling, and Jean G. Riess*

Received November 6, 1985

The reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with bicyclic amino phosphorane ligands in the Rh/ligand ratio 2/1 was shown to lead to the unusual single-chloro-bridged Rh_2 complex 1.¹

The novel characteristics of 1 lie in its having a single bridging chlorine atom between the two metal atoms, which are both in a formal oxidation state of I, and the nonsymmetric substitution of the two Rh atoms, whose actual charges are therefore different.

Complex 1 was expected to exhibit considerable reactivity, especially toward nucleophiles and small unsaturated molecules.

- (1) Wachter, J.; Jeanneaux, F.; Le Borgne, G.; Riess, J. G. *Organometallics* **1984**, *3*, 1034.
 (2) Deeming, A. J. *J. Organomet. Chem.* **1979**, *175*, 105.
 (3) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21.

We report here our investigations, whose results are summarized in Scheme I.

Experimental Section

Melting points were determined with a Reichert microscope in sealed capillaries. Elemental analyses were performed by the Centre de Microanalyses du CNRS. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer, ¹H, ³¹P, and ¹⁹F NMR spectra on a Bruker WH-90 or a Bruker 80 instrument, and ¹³C and natural-abundance INEPT ¹⁵N NMR spectra on a Bruker WM 400 spectrometer (100.62 and 40.56 MHz, respectively). ¹J_{N-H} (73.5 Hz) is the driving coupling in the INEPT experiment.¹⁰ Chemical shifts are given in ppm downfield from internal tetramethylsilane (¹H and ¹³C), external 85% H₃PO₄ (³¹P), internal CFCl₃ (¹⁹F), and external 80/20 (v/v) MeNO₂ in C₆D₆ (¹⁵N). All experimental procedures were carried out under oxygen-free argon. The solvents were freshly distilled under argon from appropriate drying agents.

Synthesis of $(t\text{-BuNC})_2(\text{Cl})\text{Rh}(\mu\text{-Cl})\text{Rh}(\text{CO})[\text{PhP}(\text{OC}(\text{CH}_3)_2\text{CH}_2)_2\text{NH}]$ (2). A solution of 26.5 mg (0.32 mmol) of *t*-BuNC in 2 mL of toluene was added to a solution of 1 (100 mg, 0.16 mmol) in 6 mL of toluene with stirring at 0° C. After 1 h, the solution was allowed to warm to room temperature. Evaporation of the solvent led to a pale yellow powder, which was washed with pentane (3 × 10 mL). Recrystallization from a 1/1 mixture of THF/pentane at -30° C gave 103 mg (0.135 mmol, 85%) of 2 as yellow crystals containing 1/3 mol of THF/mol of 2, confirmed by ¹H NMR; mp 185° C. IR (KBr, cm⁻¹): ν(NH) 3260, ν(NC) 2180, ν(CO) 1990, ν(RhCl) 320 and 300. ³¹P{¹H} NMR (THF): 147.5 (d, ¹J_{P-Rh} = 178.6 Hz). ¹H NMR (CDCl₃): 1.39, 2.16 (s, s; 6 H, 6 H; CH₃ exo and endo), 1.45, 1.47 (d, d; J_{Rh-H} ≈ 2 Hz; 9 H, 9 H; *t*-Bu), 2.76, 2.79, 3.33, 3.41 (d, d, d, d; 1 H, 1 H, 1 H, 1 H; ²J_{CH-H} = 14 Hz; CH exo and endo). ¹³C NMR (CD₂Cl₂): 190.1 (dd, ¹J_{Rh-C} = 93 Hz, ²J_{P-C} = 16 Hz, CO), 182.6 (d, ¹J_{Rh-C} = 70 Hz, C=N), 135.5 (d, ¹J_{P-C} = 92 Hz, P-C(Ph)), 132.2 (s, *p*-C(Ph)), 130.0 and 128.8 (d, d; J_{P-C} = 15 Hz, J_{P-C} = 13 Hz; *o*- and *m*-C(Ph)), 81.5 (s, O-C), 61.8 (d, J_{P-C} = 8 Hz, N-CH₂), 58.4 (s, =N-C), 31.7 and 31.0 (s, d; J_{P-C} = 6 Hz; O-C(CH₃)₂), 30.4 (s, N-C(CH₃)₂). INEPT ¹⁵N NMR (CD₂Cl₂): -370 (ddd, ¹J_{N-H} = 73.5 Hz, ¹J_{N-Rh} ≈ ²J_{N-P} = 11.8 Hz). Anal. Calcd for C₂₂H₄₀Cl₂N₃O₃PRh₂·1/3 THF (*M*_r = 762.0): C, 41.46; H, 5.60; N, 5.41. Found: C, 41.39; H, 5.55; N, 5.41.

Synthesis of $(\text{CO})(\text{Cl})\text{Rh}(\mu\text{-Cl})(\mu\text{-R}'\text{C}=\text{CR}')(\mu\text{-CO})\text{Rh}[\text{PhP}(\text{OC}(\text{CH}_3)_2\text{CH}_2)_2\text{NH}]$. R' = CO₂Me (DMA), 3a. A solution of DMA (1 mL) in toluene (0.036 M) was added, at room temperature with stirring, to a solution of 1 (23 mg, 0.036 mmol) in 3 mL of toluene. After 3 h, the yellow precipitate was filtered, washed with pentane, and dried under vacuum, leading to 2k mg (0.032 mmol, 89%) of 3a. 3a is insoluble in toluene, THF, CHCl₃, CH₂Cl₂, and ether and sparingly soluble in CH₃CN, DMF, and Me₂SO, in which it decomposes. IR (KBr, cm⁻¹): ν(NH) 3220, ν(C=O) 2085 and 1785, ν(C=O) 1695, ν(C≡C) 1555, ν(Rh-Cl) 300 and 290. Anal. Calcd for C₂₂H₂₈Cl₂NO₈PRh₂·1/3 C₆H₅CH₃ (*M*_r = 772.67): C, 37.79; H, 3.97; N, 1.81; P, 4.01. Found: C, 37.64; H, 3.96; N, 1.80; P, 3.85.

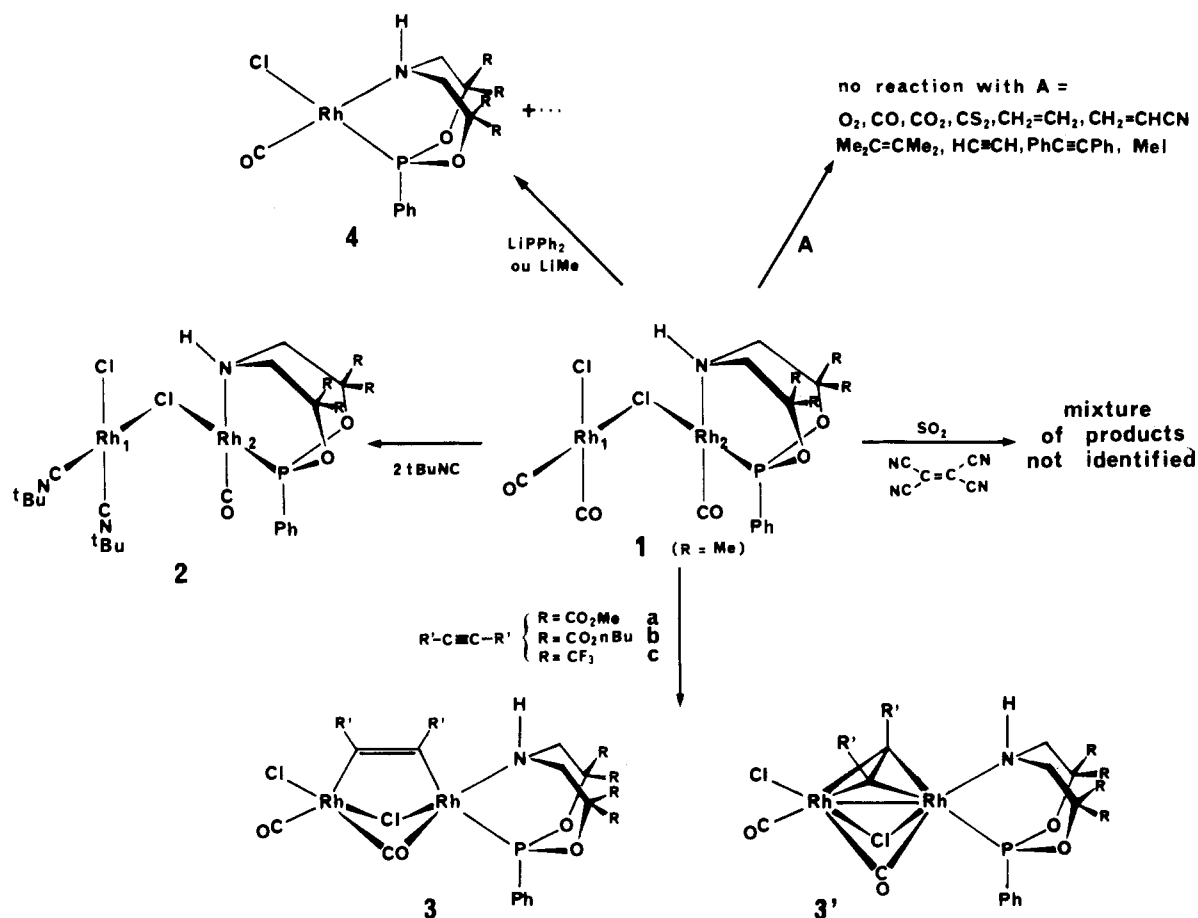
R' = CO₂-*n*-Bu (DBA), 3b. Similarly, 3b was obtained in 88% yield as a yellow powder, soluble in CH₂Cl₂ and CHCl₃ and sparingly soluble in toluene and THF. IR (KBr, cm⁻¹): ν(NH) 3220, ν(C=O) 2085 and 1785, ν(C=O) 1695, ν(C≡C) 1555, ν(Rh-Cl) 300 and 290. ³¹P{¹H} NMR (CH₂Cl₂): 147.2 (dd, ¹J_{P-Rh} = 229 Hz, ²J_{P-Rh} = 9 Hz). ¹H NMR (CDCl₃): 0.90-1.50 (m, CH₂CH₃ and O-C(CH₃)₂), 2.90-4.3 (m, NCH₂ and OCH₂), 6.50 (m, NH), 7.5 (m, C₆H₅). Anal. Calcd for C₂₈H₄₀Cl₂NO₈PRh₂ (*M*_r = 826.4): C, 40.66; H, 4.84; N, 1.69, P, 3.75. Found: C, 40.73; H, 4.80; N, 1.62; P, 3.72.

R' = CF₃ (HFB), 3c. Gaseous HFB was bubbled for 1/2 h through a magnetically stirred solution of 1 (80 mg, 0.127 mmol) in 10 mL of THF. Evaporating the solvent, washing with pentane, and drying under vacuum led to 3c as a yellow powder (83 mg, 0.109 mmol, 86%), sparingly soluble in CH₂Cl₂ and CHCl₃. IR (KBr, cm⁻¹): ν(NH) 3220, ν(C=O) 2100 and 1790, ν(C≡C) 1575, ν(Rh-Cl) 310 and 300. ³¹P{¹H} NMR (CH₂Cl₂): 145 (dm, ¹J_{P-Rh} = 220 Hz). ¹⁹F NMR (CDCl₃): -50.6 (m, 3 F), -53.0 (dq, ³J_{F-F} = 12 Hz, ³J_{F-Rh} = 3 Hz, 3 F). Anal. Calcd for C₂₀H₂₂Cl₂F₆NO₈PRh₂·0.6 THF (*M*_r = 762): C, 33.38; H, 3.33; F, 14.16; N, 1.74; P, 3.85. Found: C, 33.39; H, 3.43; F, 14.80; N, 1.69; P, 3.86. The presence of THF is further confirmed by ¹H NMR.

Results and Discussion

Action of *tert*-Butyl Isocyanide. Allowing 1 equiv of *t*-BuNC to react with 1 in toluene at room temperature leads to the substitution not of one but of two carbonyl groups, which results in a mixture of 2 and unreacted 1 in a 1/1 ratio. Under these conditions, a ν(C≡N) stretch at 2190 cm⁻¹ and a new ν(C=O)

Scheme 1



vibration at 1995 cm^{-1} are found in the IR spectrum of the reaction solution, together with those belonging to **1** (2050 and 2020 cm^{-1}). The addition of a further 1 equiv of *t*-BuNC results in the disappearance of the vibrations characteristic of **1** and allows the isolation of **2** in 85% yield as yellow crystals whose structure is established by its analytical and spectroscopic data.

Coordination by phosphorus is evidenced by the presence of a doublet at 147.5 ppm ($J_{\text{P-Ph}} = 179\text{ Hz}$) in the ^{31}P NMR spectrum of **2**. The presence in the IR spectrum of a $\nu(\text{NH})$ stretch at 3260 cm^{-1} together with the INEPT ^{15}N NMR spectrum, which shows the ^{15}N atom to be coupled with both the ^{109}Rh and ^{31}P atoms ($J_{\text{N-Rh}} \approx J_{\text{N-P}} \approx 12\text{ Hz}$), confirms nitrogen and phosphorus coordination on the same Rh atom. In addition, the ^1H NMR spectrum of **2** exhibits two doublets at 1.45 and 1.47 ppm ($J_{\text{H-Rh}} \approx 2\text{ Hz}$) for the *t*-BuNC groups and two singlets at 2.16 and 1.39 ppm for the methyl groups of the amino phosphane ligand: both groups of signals are in the 3/2 ratio expected for structure **2**. An isomeric structure, **2'**, containing one *t*-BuCN on each Rh atom and the CO ligand on one Rh and the amino phosphane ligand on the other Rh atom, can further be eliminated on the basis of the ^{13}C NMR spectrum. This exhibits, in agreement with structure **2**, a doublet of doublets for the CO carbon at 190.1 ppm ($J_{\text{C-Rh}} = 83\text{ Hz}$ and $J_{\text{C-P}} = 16\text{ Hz}$), showing that the CO and P sites are coordinated on the same Rh atom (for structure **2'**, we expect one doublet ($J_{\text{Rh-C}}$ coupling only) for this CO carbon). The fact that only one doublet at 182.6 ppm ($J_{\text{C-Rh}} = 70\text{ Hz}$) is detected for the two isocyanide carbon atoms, while two signals appear for the *t*-Bu groups in the ^1H NMR, is taken to indicate that their ^{13}C chemical shifts are too close to be separated, even at 100.62 MHz .

If the reaction is performed with an excess of *t*-BuNC (more than 8 equiv), quantitative formation of the known derivative $[\text{Rh}(\text{t-BuNC})_4]^+\text{Cl}^-$ is observed. Adding 1 equiv of *t*-BuNC to

2 leads to the formation of a mixture of compounds, from which $[\text{Rh}(\text{t-BuNC})_4]^+\text{Cl}^-$ could be isolated: substitution of the third CO group is thus in competition with other ligand substitutions, and particularly with the Rh-Cl-Rh bridge cleavage (similar competitive substitutions and bridge cleavage have also been observed when $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ is allowed to react with 1 equiv or more of *t*-BuNC).²

Action of Alkynes. Complex **1** reacts only with alkynes ($\text{R}'\text{C}\equiv\text{CR}'$) activated by electron-withdrawing groups such as $\text{CO}_2\text{R}''$ or CF_3 . No reaction is observed with acetylene or diphenylacetylene under thermal or photolytic conditions. Thus, allowing **1** to react with 1 equiv of DMA ($\text{R}' = \text{CO}_2\text{Me}$), DBA ($\text{R}' = \text{CO}_2\text{-}n\text{-Bu}$), or HFB ($\text{R}' = \text{CF}_3$) leads to the quantitative formation of derivatives **3a-c**, respectively, as yellow powders.

In bimetallic complexes, the alkynes commonly adopt two bonding modes: the tetrahedral $\mu\text{-}\eta^2$ geometry, as in **3'**, and the cis-dimetalated olefinic $\mu\text{-}\eta^1, \eta^1$ geometry, as in **3**.⁵ In the case of dinuclear Rh complexes, the $\mu\text{-}\eta^1, \eta^1$ mode is the most frequently observed;^{5,6} two examples involving the $\mu\text{-}\eta^2$ structure are also known.⁷ All the analytical and spectroscopic data collected on the isolated materials are in agreement with structure **3** rather than **3'**. The infrared data are very similar for **3a-c**, suggesting that these three derivatives have the same structure. The $\nu(\text{NH})$ stretch at 3220 cm^{-1} for **3a-c** is characteristic of N-coordination. The presence of two $\nu(\text{RhCl})$ bands at 300 and 290 cm^{-1} (310 and 300 cm^{-1} for **3c**) suggests that the Cl-Rh-Cl-Rh sequence

(4) Branson, P. R.; Green, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1303.

(5) Cowie, M.; Southern, T. *Inorg. Chem.* **1982**, *21*, 246 and references therein.

(6) (a) Corrigan, P. A.; Dickson, R. S.; Johnson, S. H.; Pain, G. N.; Yeah, M. *Aust. J. Chem.* **1982**, *35*, 2203. (b) Cowie, M.; Dickson, R. S.; Haines, B. W. *Organometallics* **1984**, *3*, 1879.

(7) (a) Dickson, R. S.; Pain, G. N.; Mackay, M. F. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2321. (b) Bennet, M. A.; Johnson, R. N.; Robertson, G. B.; Turney, T. W.; Whimp, P. O. *Inorg. Chem.* **1976**, *15*, 97.

is preserved. The vibrations at 2090 and 1785 cm^{-1} (2100 and 1795 cm^{-1} for **3c**) correspond respectively to a terminal and a bridging carbonyl group; the former is further coordinated to the Rh atom that does not bear the amino phosphane ligand (in the case where the CO and amino phosphane are coordinated on the same Rh atom, a lower value of $\nu(\text{C}=\text{O})$, close to those measured for **4** or **2**, is expected). Coordination of the alkynes is shown by the presence of the $\nu(\text{C}\equiv\text{C})$ vibration at 1550 cm^{-1} (1575 cm^{-1} for **3c**), in the region generally attributed to alkynes bridging two Rh atoms in the coordination modes $\mu\text{-}\eta^1, \eta^1$ ^{5,6} and $\mu\text{-}\eta^2, \eta^2$ ⁷ and as such, IR spectroscopy does not allow distinction between these two coordination modes. Higher values for the $\nu(\text{C}\equiv\text{C})$ vibration, from 1850 to 1950 cm^{-1} , are found for alkynes π -coordinated to one rhodium center only,⁸ thus excluding such a structure for the materials isolated here.

The poor solubility and poor stability of **3b,c** prevented us from measuring satisfactory ¹³C NMR spectra, even at 100.62 MHz on a Bruker WM 400 spectrometer with a S/N ratio sufficient to detect with confidence the Rh-C couplings, which would have allowed us to distinguish unambiguously between structures **3** and **3'**. However, the ¹H, ³¹P, and ¹⁹F NMR data could be collected for **3b,c**, but not for **3a**, whose solubility is very low and is further accompanied by decomposition. The ³¹P NMR spectra of **3b,c** consist respectively of a doublet of doublets centered at 147 ppm (¹J_{P-Ph} = 230 Hz, ^xJ_{P-Rh} = 9 Hz) and of a complex doublet at 145 ppm (¹J_{P-Rh} = 220 Hz) due to additional coupling with the ¹⁹F nuclei. The largest coupling constants indicate P-coordination. In the case of **3b**, assignment of the other coupling constant to ³J_{P-Rh} through a Rh-Rh bond is only tentative, as high-order coupling constants have been measured for dinuclear Rh species in which no such bonds occur.⁹ More informative, the ¹⁹F NMR spectrum of **3c** exhibits a complex multiplet at -50.6 ppm and a doublet of quadruplets at -53 ppm ($J_{\text{F-F}} = 12$ Hz; $J_{\text{F-Rh}} = 3$ Hz) in a 1/1 ratio. This pattern and, particularly, the different fine structures for the two F resonances favor the less symmetrical structure **3e** with respect to the almost symmetrical structure **3'c** (for which identical fine structures would have been expected for each CF₃ group).

Action of the Strong Nucleophiles MeLi and Ph₂PLi. The action of MeLi or Ph₂PLi on **1** provokes the cleavage of the chloro bridge: from the reaction mixture, only the known mononuclear complex **4**¹ could be isolated (60% yield).

Action of Other Small Molecules. A rapid reaction with total consumption of **1** is observed with SO₂ or (CN)₂C=C(CN)₂ (TCNE) in toluene, but all attempts to isolate any pure compound have so far failed.

No reaction of **1** is observed with an excess of O₂, CO, CO₂, CS₂, or MeI or of unactivated or moderately activated alkenes (H₂C=CH₂, H₂C=CHCN, Me₂C=CMe₂) under thermal or photolytic conditions at atmospheric pressure.

Conclusions

The main feature of this study is the unexpected inertia of the singly bridged dissymmetric binuclear rhodium complex **1**. Its absence of reactivity toward O₂, CO, CO₂, and MeI is surprising, as is its limited tendency to add alkenes and alkynes and form additional bridges, which occurs only with the most strongly activated ones to yield the $\mu\text{-CO}$, $\mu\text{-Cl}$, and $\mu\text{-}\eta^1, \eta^1$ triply bridged species **3**. The stability of the single chloro bridge in **1** is illustrated by the fact that it is preserved in the presence of *t*-BuNC, which leads to the substitution of the two carbonyl groups located on the same metal center. To cleave this bridge requires an excess of *t*-BuNC, an excess of the bidentate P/N ligand,¹ or the action of strong nucleophiles such as MeLi and Ph₂PLi.

Contribution from the Department of Chemistry, University of California, Davis, California 95616

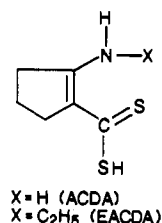
A 1,1-Dithiocarboxylate Ligand with an Easily Derivatizable Group. Synthesis and Structure of Tris[2-(ethylamino)cyclopent-1-ene-1-dithiocarboxylato]bismuth(III)

Parimal K. Bharadwaj and W. Kenneth Musker*

Received October 31, 1986

1,1-Dithio ligands (dithiocarbamates, dithiophosphates, dithioxanthates, dithiocarboxylates) have been the subject of intense investigation over the last two decades.¹ Most studies are concerned with transition-metal complexes of 1,1-dithio ligands having only alkyl or aryl substituents. Only a few examples of complexes of 1,1-dithio ligands are known in which the ligand has free functional groups not involved in coordination.

2-Aminocyclopent-1-ene-1-dithiocarboxylic acid (ACDA), a compound having antifungal properties,² forms complexes^{3,4} with



transition metals (Ni(II), Pt(II), Pd(II), Mo(VI)) that were believed to be monomeric, neutral species with S,S rather than N,S bonding to the metal. However, no crystallographic information on any of these complexes was obtained because of their limited solubility in common organic solvents. However, it is easy to derivatize the amine group of the ligand by transamination reactions to give species having a variety of substituents at the nitrogen atom. These derivatives give complexes with improved solubility characteristics. As part of a research program to develop a radiopharmaceutical that can bind strongly to both Pb(II) and Bi(III) and, in addition, have latent functionality to bind to a suitable carrier, we have prepared and determined the crystal structure of the Bi(III) complex of 2-(ethylamino)cyclopent-1-ene-1-dithiocarboxylic acid (EACDA). This also appears to be the first crystal structure of a dithiocarboxylate complex with a non transition metal that has been reported.

Experimental Section

Chemicals Used. All of the reagent grade chemicals were purchased from Aldrich Chemical Co. and were used without further purification. Anhydrous BiCl₃ was 98% pure.

1. Preparation of 2-Aminocyclopent-1-ene-1-dithiocarboxylic Acid (ACDA). ACDA was prepared by following a published procedure.³ Yield: 65% (mp 97-98 °C (lit.³ 98 °C)).

2. Preparation of 2-(Ethylamino)cyclopent-1-ene-1-dithiocarboxylic Acid (EACDA). EACDA was prepared from ACDA by a transamination reaction with ethylamine following a published procedure.^{2b} The product was recrystallized from acetone. Yield: 81%. (mp 111-112 °C (lit.^{2b} 111 °C)).

3. Preparation of Bi(III) Complexes. (a) With ACDA. Complex I. An ethanolic solution of anhydrous BiCl₃ (0.32 g; 1 × 10⁻³ mol) (10 mL) was added slowly with constant stirring at room temperature to an ethanolic solution (10 mL) of ACDA (0.48 g; 3 × 10⁻³ mol). The bismuth complex was obtained immediately as an orange precipitate. The pre-

- (8) Van Gaal, H. L. M.; Graef, M. W. M.; Van der Ent, A. *J. Organomet. Chem.* **1977**, *131*, 453.
 (9) (a) Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060. (b) Mague, S. T.; De Vries, S. H. *Inorg. Chem.* **1982**, *21*, 1632.
 (10) The INEPT experiment has been performed according to: Van Stein, G. C.; Van Koten, G.; Vrieze, K.; Breward, C.; Spek, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4486.

- (1) Concouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301-469 and references cited therein.
 (2) (a) Takeshima, T.; Yokoyama, M.; Imamoto, T.; Akano, M.; Asaka, H. *J. Org. Chem.* **1969**, *34*, 730. (b) Bordas, B.; Sohar, P.; Matolcsy, G.; Berensci, P. *J. Org. Chem.* **1972**, *37*, 1727.
 (3) Nag, K.; Joardar, D. S. *Inorg. Chim. Acta* **1975**, *14*, 133.
 (4) Chaudhury, M. *Inorg. Chem.* **1984**, *23*, 4434.
 (5) See paragraph at end of paper regarding supplementary material.
 (6) Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1976**, 791.
 (7) Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 2425.