an excess of acetic anhydride (1 mL, 10 mmol), to obtain complete acetylation of the amino groups. The control silica gel was processed as described earlier. C) Naphthalene/silica gel: The same procedure was used as for theophylline/silica gel (A), but using 2-naphthylacetic acid (186 mg, 1 mmol) instead of 8-carboxypropyltheophylline.

Preparation of the polymers: A pre-polymerization mixture consisting of DVB (2.14 mL, 12 mmol), TFMAA (336 mg, 2.4 mmol), and 2,2′-azobis(2,4-dimethylvaleronitrile) (20 mg) was prepared in a glass vial. According to the pore volume of the silica (ca. 0.65 mL g^{-1}), the amount of the mixture required to fill the pores was added to the silica gel (theophylline/silica gel, control silica gel, or naphthalene/silica gel) and gently stirred with a stainless steel spatula.[11] The vial was flushed gently with N_2 for 2 min and the mixture was then allowed to polymerize overnight at 45 °C. After polymerization was completed (this was monitored by polymerizing a portion of the pre-polymerization mixture without silica gel) the polymer/silica gel composite was gently wet-milled in acetone with a manual mortar and pestle to disintegrate any particle aggregates. The composite was then transferred into a plastic tube with a screw cap, suspended in acetone (2 mL), and cooled in a water/ice bath. Aqueous HF (4 mL, 40 %) was added portionwise whilst shaking the mixture to dissolve the silica matrix of the composite. The suspension was then allowed to react overnight on a rocking-table at room temperature. The remaining polymer was washed extensively on a G4-glass filter funnel with 20 % acetone in deionized water (ca. 2 L) until the filtrate had a neutral pH value, and finally washed with methanol (0.25 L). The polymer particles were then dried in an oven at 45 °C for 6 h and in vacuo for a further 6 h.

Elemental analysis: Flash combustion elemental analysis coupled to gas chromatography was performed at MikroKemi AB (Uppsala, Sweden).

Radioligand binding assays: The polymer particles were suspended in toluene and appropriate volumes were added into 1.5-mL polypropylene test tubes, followed by the radioligand [^{3}H]-theophylline, varying amounts of a solution of a competing ligand if appropriate, and toluene to give a total volume of 1 mL. The samples were incubated on a rocking-table for 12 h at room temperature. Particles were removed by centrifugation and supernatant (500 μL) was withdrawn and added to scintillation liquid (10 mL, Ecoscint O, National Diagnostics, Atlanta, GA, USA). The radioactivity was measured by liquid scintillation counting with a Rackbeta 1219 counter (LKB Wallac, Turku, Finland). This assay is similar to that described previously.[12]

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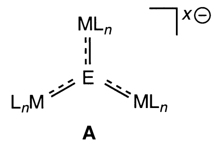
Synthesis and Reactivity of [{(CO)$_5$Cr}$_3$Pb]$^{2-}$, an Unsaturated Compound with Trigonal-Planar Coordinated Lead

Peter Rutsch und Gottfried Huttner*

Dedicated to Professor Arndt Simon on the occasion of his 60th birthday

Compounds **A**, which contain a main group element bound in a trigonal-planar environment to three organotransition metal 16-valence electron fragments L_nM (e.g. $L_nM = (CO)_4Fe$, E = In, $x = 3$;[1] $L_nM = (CO)_4Fe$, E = Sn, Pb, $x = 2$;[2] $L_nM = (CO)_5Cr$, E = Sn, $x = 2$;[3] $L_nM = (CO)_5Cr$, E = Sb, $x = 1$;[4] $L_nM = Cp(CO)_2Mn$, E = Te, $x = 0$[5]), are in the broadest sense isoelectronic analogues of well known four-center, six-π-electron systems such as NO_3^- and CO_3^{2-}. The $p_\pi - p_\pi$ interaction in systems such as CO_3^{2-} corresponds to the metal – d_π-main group element – p_π interaction in the organometal derivatives.[6] The unsaturated character of these organometallic π systems becomes apparent from the short M–E bonds[1–5] as well as from their spectroscopic behavior.[3] The NMR signals of the trigonal-planar coordinated main group elements are each shifted to low field.[3, 7] This is also true for **1**, which is obtained from the reaction of disodium decacarbonyldichromate with lead nitrate [Eq. (1)]. The ^{207}Pb NMR signal of **1** is shifted to low field at $\delta = 7885$ and supports, in agreement with the structural data (Figure 1),[8] the unsaturated character of **1**.



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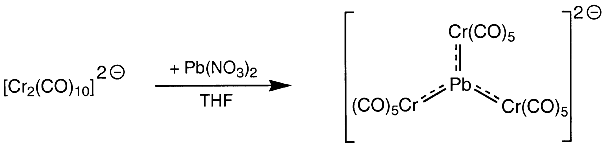

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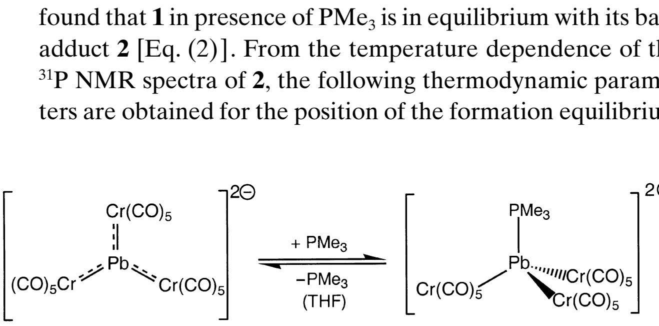
(1)

Chemical evidence for the unsaturated character of π systems of the type **A** was hitherto unknown. We have now found that **1** in presence of PMe_3 is in equilibrium with its base adduct **2** [Eq. (2)]. From the temperature dependence of the ^{31}P NMR spectra of **2**, the following thermodynamic parameters are obtained for the position of the formation equilibrium



1 **2**

(2)

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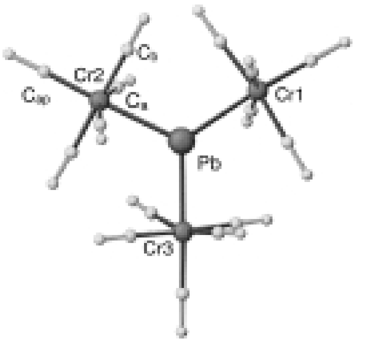

Figure 1. Structure of **1** in the crystal of $[(PPh_4)^+]_2 \cdot \mathbf{1}$.[8] Selected bond lengths [pm] and angles [°]: Pb-Cr1 273.3(1), Pb-Cr2 272.6(1), Pb-Cr3 272.8(1), Cr-C_a 184.5(1) – 188.5(1), Cr-C_b 186.1(1) – 190.0(3), Cr-C_{ap} 183.8(2) – 185.7(3); Cr1-Pb-Cr2 119.7(6), Cr1-Pb-Cr3 120.8(6), Cr2-Pb-Cr3 117.9(5), C_a-Cr-C_a 160.0(4) – 169.0(6), C_b-Cr-C_b 172.1(6) – 176.5(6); torsion angle τ [°]: X-Pb-Cr-C_a 18 – 26 (the reference atom X is located on a reference axis that runs through the lead center and is perpendicular to the plane Cr1-Cr2-Cr3).

of $[(PPh_4)^+]_2 \cdot \mathbf{2}$: $K_{298} = 1.86$, $\Delta H = -(59 \pm 2)\,\mathrm{kJ\,mol^{-1}}$, $\Delta S = (-194 \pm 9)\,\mathrm{J\,mol^{-1}\,K^{-1}}$. Whereas accordingly in equimolar mixtures of **1** and PMe_3, **2** is only formed quantitatively at temperatures below 213 K (within the accuracy of the NMR experiment), the tetraphenylphosphonium salt of **2** can be crystallized from THF/EtOH already at room temperature. The structure analysis of **2** (Figure 2) confirms the coordination of the Lewis base PMe_3 to the coordinatively unsaturated lead center.[8] The Pb–P distance of 284 pm lies in the usual range.[9] The $^2J_{P,Pb}$ coupling of 1567 Hz observed in the ^{31}P NMR spectrum supports this finding.[9] Whereas in **1** the lead center lies approximately in the plane formed by the three chromium atoms (deviation 13 pm, Figure 1), in **2** it lies 38 pm above this plane, and in fact on the side facing the ligand (Figure 2 a). The angles Cr-Pb-Cr (117°) and P-Pb-Cr (101°) deviate, however, strongly from the values expected for an ideal tetrahedron; through the addition of the Lewis base PMe_3 the trigonal-planar coordination of the central element lead in **1** (Figure 1) is only slightly pyramidalized.[10]

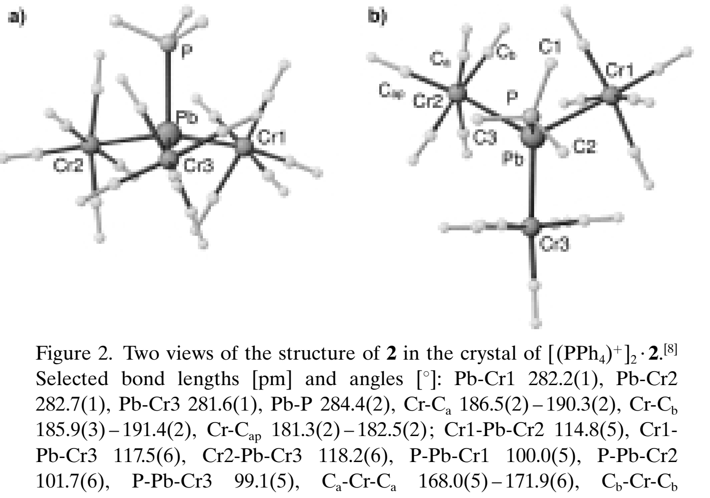

Figure 2. Two views of the structure of **2** in the crystal of $[(PPh_4)^+]_2 \cdot \mathbf{2}$.[8] Selected bond lengths [pm] and angles [°]: Pb-Cr1 282.2(1), Pb-Cr2 282.7(1), Pb-Cr3 281.6(1), Pb-P 284.4(2), Cr-C_a 186.5(2) – 190.3(2), Cr-C_b 185.9(3) – 191.4(2), Cr-C_{ap} 181.3(2) – 182.5(2); Cr1-Pb-Cr2 114.8(5), Cr1-Pb-Cr3 117.5(6), Cr2-Pb-Cr3 118.2(6), P-Pb-Cr1 100.0(5), P-Pb-Cr2 101.7(6), P-Pb-Cr3 99.1(5), C_a-Cr-C_a 168.0(5) – 171.9(6), C_b-Cr-C_b 172.0(6) – 175.8(5); torsion angle τ [°]: P-Pb-Cr-C_a 24 – 27.

Consistent with their stronger saturated character (Figure 2), the Pb–Cr bonds, which are shortened through multiple-bond contributions to 273 pm in **1** (Figure 1), are extended to 282 pm in **2**. With the reaction of **1** to give **2** and the complete characterization of both compounds, the unsaturated character of four-center, six-π-electron systems of the type **A** is now also supported by reactivity studies for one example.

Experimental Section

Experimental conditions see ref. [3], ^{207}Pb NMR spectra see ref. [9c]. C,H analyses: Mikroanalytisches Laboratorium, Organisch-Chemisches Institut der Universität Heidelberg.

Synthesis of $[PPh_4]_2[\{(CO)_5Cr\}_3Pb]$ ($[(PPh_4)^+]_2 \cdot \mathbf{1}$): $Pb(NO_3)_2$ (331 mg, 1 mmol) was added to a yellow solution of $Na_2[Cr_2(CO)_{10}]$ (860 mg, 2 mmol) in THF (50 mL) under stirring. Within 4 h the solution turned intense violet, it was filtered through 5 cm Kieselgur and concentrated to 3 mL. The chromatographic purification was carried out over 15 cm silica gel. $[Cr(CO)_6]$ and $Na_2[\{(CO)_5Cr\}_2Pb(NO_3)_2]$ (for structure see ref. [8]) were separated with THF/Et_2O (1/1). The sodium salt of **1** was eluted with EtOH as a deep purple band. After concentration, a solution of $[PPh_4]Cl$ (740 mg, 2 mmol) in ethanol was added, which led to the formation of $[PPh_4]_2[\{(CO)_5Cr\}_3Pb]$ as a black precipitate in 47 % yield (640 mg; yield based on $Pb(NO_3)_2$). The product was dissolved in THF (3 mL) and isolated, after layering with ethanol, in the form of black crystals after six days at room temperature, yield 430 mg (32 %). ^1H NMR: $\delta = 7.92 - 7.68$ (m, 40H; H_{arom}); ^{13}C NMR: $\delta = 230.8$ (s, 3C; C_{ax}), 223.2 (s, 12C; C_{eq}), 136.5 – 118.2 (m, 48 C; C_{arom}); ^{31}P NMR: $\delta = 22.5$ (s, 2P; Ph_4P); ^{207}Pb NMR: $\delta = 7885$ (s, 1Pb); IR (THF): $\tilde{\nu}(CO) = 2008$ (w), 1977 (vs), 1911 (vs), 1857 cm^{-1} (vs); UV/Vis (THF): $\lambda_{max}(\varepsilon) = 331$ (20500), 428 (5600), 534 nm (1600 $M^{-1}cm^{-1}$); elemental analysis (%): C 51.69 (calcd: 51.75), H 3.20 (calcd.: 2.75).

Synthesis of $[PPh_4]_2[\{(CO)_5Cr\}_3PbP(CH_3)_3]$ ($[(PPh_4)^+]_2 \cdot \mathbf{2}$): $[(PPh_4)^+]_2 \cdot \mathbf{1}$ (430 mg, 0.32 mmol) was dissolved in THF (4 mL) and treated with a 1.0 M PMe_3 solution in THF (1 mL, 1 mmol) under stirring. The reaction solution was layered with ethanol; after five days $[(PPh_4)^+]_2 \cdot \mathbf{2}$ (270 mg) was obtained in the form of black crystals (60 %, based on $[(PPh_4)^+]_2 \cdot \mathbf{1}$). ^1H NMR: $\delta = 7.92 - 7.68$ (m, 40H; H_{arom}), 1.07 (s, 9H; CH_3); ^{13}C NMR: $\delta = 231.1$ (s, 3C; C_{ax}), 223.8 (s, 12C; C_{eq}), 136.4 – 118.2 (m, 48C; C_{arom}), 15.5 (s, 3CH_3); ^{31}P NMR (25 °C): $\delta = 22.5$ (s, 2P; Ph_4P), -114.3 (s, 1P, $P(CH_3)_3$); ^{31}P NMR (-90 °C): $\delta = 22.5$ (s, 2P; Ph_4P), -180.06 (s, $^2J_{P,Pb} = 1567$ Hz, 1P, $P(CH_3)_3$); ^{207}Pb NMR (-90 °C): $\delta = 7813$ (s, 1Pb); IR (THF, 25 °C): $\tilde{\nu}(CO) = 1977$ (vs), 1907 (vs), 1857 cm^{-1} (vs); UV/Vis (THF, 25 °C): $\lambda_{max}(\varepsilon) = 327$ (19800), 428 (5100), 541 nm (1400 $M^{-1}cm^{-1}$); elemental analysis (%): C 51.53 (calcd: 51.53), H 3.61 (calcd: 3.21).

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[8] Crystal structure data: The X-ray data were collected on a Nonius-Kappa-CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda_{Mo} = 0.71074$ Å). Data collection and reduction were performed with the Nonius software,[11] the structure solution and refinement were carried out with the SHELXTL-PLUS software package; the structures were

solved by direct methods with SHELXS-86 and refined with SHELXL-93.[12] The program XPMA was used for the graphical processing of the data.[13] The figures were produced with WINRAY-32.[14] The refinement was carried out anisotropically against F^2, hydrogen atoms were included in calculated positions. **1**: space group $P2_1/c$, $a = 1277.4(3)$, $b = 1956.0(4)$, $c = 2436.8(5)$ pm, $\beta = 103.63(3)^\circ$, $V = 5917 \times 10^6$ pm^3, $\rho_{calcd} = 1.641$ g cm^{-3}, $2\theta_{max} = 52.1^\circ$, $Z = 4$, 71438 measured reflections, 11474 independent reflections, of which 5485 ($I > 2\sigma(I)$) observed, 758 refined parameters, $R = 0.070$, $Rw = 0.112$, max. residual electron density 1.54×10^{-6} e pm^{-3}. **2**: space group $P\bar{1}$, $a = 1422.2(3)$, $b = 1902.5(4)$, $c = 2609.1(5)$ pm, $\alpha = 100.58(3)$, $\beta = 103.63(3)$, $\gamma = 108.48(3)^\circ$, $V = 6490 \times 10^6$ pm^3, $\rho_{calcd} = 1.543$ g cm^{-3}, $2\theta_{max} = 55.0^\circ$, $Z = 4$, 58282 measured reflections, 29826 independent reflections, of which 19004 ($I > 2\sigma(I)$) observed, 1463 refined parameters, $R = 0.077$, $Rw = 0.204$, max. residual electron density 2.39×10^{-6} e pm^{-3}. The two crystallographically independent anions **2** are the same with regard to all the important structural features. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137594 (**1**), -137593 (**2**), and -137592 ($Na_2[\{(CO)_5Cr\}_2Pb(NO_3)_2]$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Metal-Based NO Sensing by Selective Ligand Dissociation**

Katherine J. Franz, Nisha Singh, and
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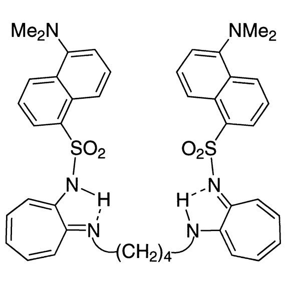
The large and increasing number of biological processes for which nitric oxide is implicated necessitates the development of improved methods of NO detection. Currently available techniques often rely on the identification of NO metabolites, such as nitrite and nitrate, or lack sensitivity.[1] The application of ratiometric biosensors[2] and ultramicro amperometric sensors[3–5] affords one avenue to obtain selective, sensitive detection of NO in vivo. Fluorescent indicators also provide desirable properties that allow direct, real-time detection with both spatial and temporal resolution,[6] as has been amply demonstrated for Ca^{II} sensors.[7] Although the invention of fluorescent NO sensors is an active research area, so far these methods rely on indirect detection of more reactive NO_x species,[8–10] display decreased fluorescence intensities upon NO binding,[11] or require further chemistry to provide a positive fluorescence response.[12, 13] We report herein an approach in which the formation of a transition metal nitrosyl complex triggers a positive fluorescent signal in response to NO.

The design of this NO sensor takes advantage of the fluorescence-quenching properties of transition metal ions with partly filled d shells. We prepared a ligand containing a fluorophore that is quenched by the metal center, in this case Co^{II}, in the absence of NO to give little residual signal for the "off" response. In the presence of NO, however, the formation of the metal–nitrosyl adduct selectively displaces a fluorescent ligand, thereby removing it from the quenching environment and turning the fluorescence "on". A similar approach was reported for an Fe^{II} complex of a quinoline pendant cyclam but the fluorescence intensity decreased in the presence of NO.[11] An analogous ligand-displacement strategy has also been applied for a pH-sensitive fluorescent probe.[14]



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In the newly designed ligand H_2DATI-4 (**1**), each aminotroponiminate (ATI) ring is modified with a dansyl fluorophore on one of the imine nitrogen atoms and linked through the other nitrogen by a 4-methylene chain to a second such chelating unit.[15] The yellow ligand **1** is rather in-

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