are found with the more coordinatively and structurally stable clusters $Rh_6(CO)_{16}$ and $Rh_4(\mu\text{-}CO)_2(\mu\text{-}Ph_2P)_4(CO)_3(Ph_3P)$.[7] The stable mononuclear square-planar complex $RhCl(CO)(Ph_3P)_2$ also shows low activity. The low activity of the rhodium clusters is surprising if one assumes that aryl group interchange occurs between vicinal metal centers as is proposed by Kaneda et al.[3] It is possible that the rhodium clusters used in this study do not promote phosphine breakdown reactions at lower temperatures, because they are more coordinatively and structurally stable species. At the higher temperatures the breakdown of these clusters to more reactive mononuclear species and/or coordinatively unsaturated clusters is facilitated.

One possible mechanism (Scheme I) assumes that with the more reactive mononuclear rhodium complexes, the initial products of oxidative addition of the phosphine aryl–phosphorus bonds to rhodium species **1** and **2** can form phosphido-bridged intermediates **3**, which can exchange their aryl- and/or phosphido-bridging groups and thereby allow scrambling.

Catalysis of this reaction is not unique to rhodium. Other group 8 transition metals show varying degrees of activity (Table II). Of the metals screened, cobalt is the most active, but with it an induction period is observed. This may be due to the time required for the formation of the active catalyst from the catalyst precursor which is the insoluble reaction product of $Co_2(CO)_8$ with phosphines. Indeed when the catalyst solution starts becoming homogeneous, the scrambling reaction begins. The activities of the ruthenium cluster $Ru_3(CO)_{12}$ and the rhodium cluster $Rh_6(CO)_{16}$ are both very low at 130 °C, but at 170 °C the ruthenium cluster is significantly more active than the rhodium cluster.

Registry No. $Rh(acac)(CO)(Ph_3P)$, 25470-96-6; $RhCl(Ph_3P)_3$, 14694-95-2; $RhCl(CO)(Ph_3P)_2$, 13938-94-8; $Rh_4(\mu\text{-}CO)_2(\mu\text{-}Ph_2P)_4(CO)_3(Ph_3P)$, 75503-69-4; $Rh_6(CO)_{16}$, 28407-51-4; $Co_2(CO)_8$, 10210-68-1; $Os_3(CO)_{12}$, 15696-40-9; $Ni(CO)_2(Ph_3P)_2$, 13007-90-4; $Pd(Ph_3P)_4$, 14221-01-3; $Ru_3(CO)_{12}$, 15243-33-1; $Rh(acac)(CO)_2$, 14874-82-9; $(C_6H_5)_3P$, 603-35-0; $(p\text{-}CH_3C_6H_4)_3P$, 1038-95-5.

Reactivity of Some Alkyls and Aryls of Rhodium and Iridium toward Carbon Dioxide. Facile Formation and X-ray Structural Characterization of the Peroxocarbonato Complex *mer*-$\overline{\mathrm{Rh}(4\text{-}\mathrm{MeC_6H_4})[\mathrm{OOC(O)O}}][\mathrm{PhP(CH_2CH_2CH_2PPh_2)_2}]$[1]

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Summary: The reactivity of several organoiridium and -rhodium compounds $M(R)(CO)(PPh_3)_2$ and $M(R)[PhP(CH_2CH_2CH_2PPh_2)_2]$ toward carbon dioxide has been investigated. The title complex was obtained by pressuring THF solutions of $Rh(4\text{-}MeC_6H_4)[PhP(CH_2CH_2CH_2PPh_2)_2]$ to 30–60 bar with reagent grade carbon dioxide probably containing trace amounts of dioxygen. It could also be prepared by allowing the rhodium(I) precursor to react with deoxygenated CO_2 and a known amount of O_2. The structure of the peroxocarbonato derivative was determined by X-ray diffraction.

The current interest in transition metal–carbon dioxide chemistry[2] prompted us to screen some of our organoiridium and -rhodium compounds $M(R)(CO)(PPh_3)_2$[3] and $M(R)[PhP(CH_2CH_2CH_2PPh_2)_2]$[4] for their ability to bind CO_2. The preliminary results of this study are summarized in Table I.

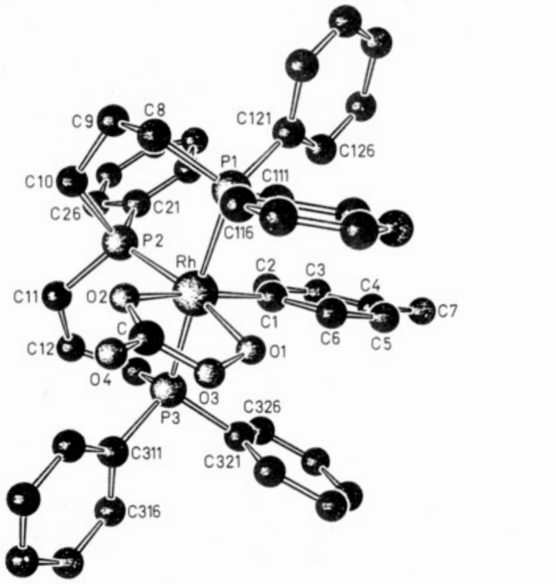

Figure 1. SCHAKAL drawing[7] of $\overline{\mathrm{Rh}(4\text{-}\mathrm{MeC_6H_4})[\mathrm{OOC(O)O}}]$-(bdpp) (**1**). Selected bond lengths (Å): Rh–P1 = 2.269 (4), Rh–P2 = 2.289 (3), Rh–P3 = 2.348 (4), Rh–O1 = 2.034 (8), Rh–O2 = 2.127 (10), Rh–C1 = 2.056 (14), O1–O3 = 1.434 (15), O2–C = 1.273 (17), O3–C = 1.320 (21), and O4–C = 1.218 (20). $\overline{\mathrm{RhOOC(O)O}}$ bond angles (deg): O1–Rh–O2 = 77.3 (4), Rh–O2–C = 112.6 (10), O2–C–O3 = 121.3 (14), C–O3–O1 = 114.7 (10); O3–O1–Rh = 112.3 (7), O2–C–O4 = 125.6 (16), and O4–C–O3 = 112.9 (13).

Although most of the complexes investigated failed to react with reagent grade CO_2 at ambient conditions, CO_2 fixation was observed to proceed when THF solutions of these compounds were exposed to gas pressures of 30–60 bars for several hours at room temperature. However, of the complexes listed in Table I, $Rh(4\text{-}MeC_6H_4)(bdpp)$[4] only was found to bind carbon dioxide in a reproducible fashion. Elemental analyses of the materials obtained indicated the stoichiometry "$Rh(4\text{-}MeC_6H_4)(bdpp)\cdot CO_4$", suggesting that transformation of the rhodium(I) aryl to a peroxocarbonate of rhodium(III), viz., $Rh(4\text{-}MeC_6H_4)(O_3CO)(bdpp)$ (**1**), had occurred.[5]

1 is practically insoluble in all common hydrocarbons, ethers, alcohols, and ketones. It is readily decomposed by chlorinated solvents such as CH_2Cl_2 and $CHCl_3$. Solution

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[1] Part 18 of the series: "Alkyl and Aryl Compounds of Iridium and Rhodium"; simultaneously part 6 of "Oligophosphine Ligands". For parts 17 and 5, respectively, see ref 4b.

[2] For recent reviews cf.: (a) Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57. (b) Floriani, C. *Pure Appl. Chem.* **1982**, *54*, 59. (c) Sneeden, R. P. A. In Wilkinson, G., Stone, F. G. A.; Abel, E. W., Eds. "Comprehensive Organometallic Chemistry"; Pergamon Press: Oxford and New York, 1982; Vol. 8, pp 225. (d) Walther, D.; Dinjius, E. *Z. Chem.* **1983**, *23*, 237.

[3] (a) Dahlenburg, L.; Nast, R.; *J. Organomet. Chem.* **1976**, *110*, 395. (b) Dahlenburg, L.; Mirzaei, F.; Yardimcioglu, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 310.

[4] (a) Arpac, E.; Dahlenburg, L. *J. Organomet. Chem.* **1983**, *241*, 27. (b) Arpac, E.; Dahlenburg, L. *Ibid.* **1983**, *251*, 361. $PhP(CH_2CH_2CH_2PPh_2)_2$ is abbreviated as "bdpp" hereafter.

[5] In a typical experiment carried out under an atmosphere of carbon dioxide (purity ca. 99.5%), a 1-g (1.32-mmol) sample of $Rh(4\text{-}MeC_6H_4)(bdpp)$ was dissolved in 10 mL of THF in a 50-mL Schlenk tube that was subsequently placed into a 250-mL steel autoclave. The vessel was pressurized to 45 bar of CO_2 and the solution stirred for 24 h at room temperature. After the carbon dioxide was vented a lemon yellow powdery precipitate of complex **1** was isolated by addition of hexane and filtration, washed with hexane, and dried in vacuo; yield 813 mg (74%). Anal. Calcd for $C_{44}H_{44}O_4P_3Rh$: C, 63.46; H, 5.33; O, 7.69; P, 11.16; Rh, 12.36. Found: C, 63.55; H, 5.29; O, 8.60; P, 11.05; Rh, 12.41.

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Table I. Reactivity of Selected Alkyls and Aryls of Iridium and Rhodium toward Carbon Dioxide

complexes studied	reactn with CO_2 at normal conditns	reactn with CO_2 under pressure (30–60 bar)
$Ir(R)(CO)(PPh_3)_2$ ($R = CH_2SiMe_3$, 4-MeC_6H_4)	gas absorption not observed	incorporation of CO_2 proceeded readily (IR); products were however found to consist of unseparable mixtures of varying composition
$Rh(R)(CO)(PPh_3)_2$ ($R = CH_2SiMe_3$, CH_2CMe_3, 4-MeC_6H_4)	not studied	vide supra
$Ir(CH_2SiMe_3)(bdpp)$[a]	gas absorption observed; product too unstable for conclusive characterization	vide supra
Rh(4-MeC_6H_4)(bdpp)[a]	gas absorption not observed	formation of Rh(4-MeC_6H_4)(O_3CO)(bdpp); see text

[a] Cf. ref 4.

characterization via ^{31}P NMR spectroscopy could however be achieved in pyridine: δ(PPh) 5.5, δ(PPh_2) −0.3 (^1J(Rh–PPh) = 108 Hz, ^1J(Rh–PPh_2) = 100 Hz, and ^2J(PP) = 38 Hz (referenced to external H_3PO_4; downfield positive)). In the infrared spectrum intense absorptions at 1660 (vs) and 1255 cm^{-1} (s) were attributed to ν(CO) of the presumed O_3CO ligand of 1. No unambiguous coordination could be assigned to the central metal of 1 on the basis of the IR and NMR data available, and thus a single-crystal X-ray diffraction analysis was performed on the complex (Figure 1).[6]

To the best of our knowledge, complex 1 presents the so far only example of a transition-metal system containing a coordinated peroxocarbonato group[8] where X-ray proof of structure exists. As indicated in Figure 1, the overall molecular geometry about the central rhodium atom corresponds to distorted octahedral with the tris(phosphine) spanning meridional positions. The O_3CO ligand acts as an O,O′ bidentate, giving rise to a five-membered $\overline{\mathrm{RhOOC(O)O}}$ chelate structure with the peroxo oxygen O1 trans to the PhP fragment and the oxo oxygen O2 trans to the tolyl ring. As a consequence of the distinct trans bond weakening influence of σ-C donors, the Rh–O2 distance of 2.127 (10) Å is considerably longer than that of 2.034 (8) Å observed for Rh–O1. The O–O bond length of the peroxo moiety, 1.434 (15) Å, compares quite well with the value of 1.46 Å reported several years ago for the O–O distance of the related hydroperoxypropanolato complex $\overline{\mathrm{Pt[OOC(O)}}\mathrm{Me_2](PPh_3)_2}$.[9]

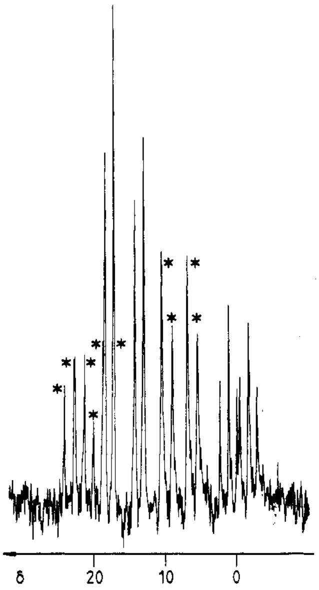

Figure 2. 36.44 MHz ^{31}P NMR spectrum of the toluene-soluble product resulting from reaction of Rh(4-MeC_6H_4)(bdpp) with rigorously deoxygenated CO_2; unlabeled lines, starting complex; transitions marked by an asterisk, "Rh(4-MeC_6H_4)(bdpp)·CO_2" (see text).

The formation of 1 most probably results from interaction of the reactants Rh(4-MeC_6H_4)(bdpp) and CO_2 with minor amounts of dioxygen fortuitously present under experimental conditions.[5] Consistently, the CO_4^{2-} complex could also be prepared by reaction of the rhodium(I) aryl with rigorously dried and deoxygenated CO_2 in the presence of a stoichiometric amount of O_2.[10]

There are two conceivable routes to the rhodium peroxocarbonato system: (1) coupling of CO_2 to a peroxo precursor as has been observed for the reactions of, e.g., $Pt(O_2)(PPh_3)_2$[8a] and $Ir(Ph)(O_2)(CO)(PPh_3)_2$,[8e] with carbon dioxide; (2) attack of dioxygen on a primary metal–carbon dioxide compound which has been reported for the formation of $Ni(O_3CO)(PCy_3)_2$ from $Ni(CO_2)(PCy_3)_2$ and O_2.[8b] In this context, the following findings derived from an initial study of the reactivity of Rh(4-MeC_6H_4)(bdpp) to-

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[6] Brittle lemon needles of 1 were grown over a period of several days from an unstirred THF solution of Rh(4-MeC_6H_4)(bdpp) pressured to 35 bar of CO_2, and a fragment of approximate dimensions 0.1 × 0.1 × 0.2 mm was chosen for X-ray work. Crystal data: from single-crystal diffractometry (Syntex $P2_1$) with Mo Kα radiation (λ = 0.71069 Å) at 291 ± 2 K; monoclinic $P2_1/n$, a = 12.217 (9) Å, b = 22.170 (11) Å, c = 14.964 (9) Å, β = 102.07 (5)°; V = 3963.4 Å^3; Z = 4; mol wt 832.66 ($C_{44}H_{44}O_4P_3Rh$); D_{calcd} = 1.396 g cm^{-3}, $F(000)$ = 1720. Data collection: Syntex $P2_1$, graphite-monochromated Mo Kα radiation; θ–2θ scan mode; 5326 data collected ($+h,+k,\pm l$; $3° \leq \theta \leq 22°$); 169 systematically absent, 4885 unique, 3206 significant, $|F_o| > 3\sigma(F_o)$; uncorrected for absorption (μ = 5.2 cm^{-1}). Structure solution and refinement: Patterson, difference-Fourier, and block-diagonal least-squares methods employing Sheldrick's SHELX program system with scattering factors from the sources given therein; anisotropic thermal parameters for all non-hydrogen atoms; hydrogens not included; R_1 = 0.078, R_2 = 0.088 (unit weights); results documented in Figure 1 and, in tabular form, in the supplementary material.

[7] Keller, E. "SCHAKAL—A Fortran Program for Graphic Representations of Molecular Models"; University of Freiburg: West Germany, 1981.

[8] For transition-metal peroxocarbonato compounds described previously cf.: (a) Hayward, P. J.; Blake, D. M.; Wilkinson,G.; Nyman, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 5873. (b) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, 708. (c) Clark, H. C.; Goel, A. B.; Wong, C. S. *J. Organomet. Chem.* **1978**, *152*, C45. (d) Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5832. (e) Mason, M. G.; Ibers, J. A. *Ibid.* **1982**, *104*, 5153.

[9] Ugo, R.; Conti, F.; Cenini, S.; Mason, R.; Robertson, G. B. *Chem. Commun.* **1968**, 1498.

[10] The intentional preparation of 1 was carried out under an atmosphere of highly purified CO_2[11] as follows: A 50-mL Schlenk tube containing 368 mg (0.49 mmol) of Rh(4-MeC_6H_4)(bdpp) in 10 mL of THF and a sealed thin-walled 11-mL ampule filled with O_2 (ca. 0.49 mmol) were placed into an autoclave. The vessel was pressurized to 60 bar of CO_2 which caused the ampule to burst, and the reaction mixture was kept under CO_2 for 24 h at room temperature. The carbon dioxide was then vented, and 1 was isolated and characterized (IR, ^{31}P NMR) as described above;[5] yield 223 mg (55%).

[11] Degree of purity: 99.995% CO_2, 0.004% N_2, and 0.001% O_2 (supplied by Rommenhöller Kohlensäurewerk, Hamburg).

ward highly purified carbon dioxide are illustrative:

Addition of hexane to THF solutions of Rh(4-MeC_6H_4)(bdpp) that had been pressured to 40–45 bar of rigorously dried and deoxygenated CO_2 afforded a yellow material, the IR spectrum of which closely resembled that of 1 except for the absence of the 1255 cm^{-1} band. Unlike 1, however, this substance turned out to be readily soluble in toluene. The ^{31}P NMR spectrum of a freshly prepared C_7H_8 solution recorded at 273 K (Figure 2) consisted of two overlapping spin systems characterized by the following: (1) $\delta(PPh_2)$ 15.9, δ(PPh) 0.2 ($^1J(Rh-PPh_2)$ = 157 Hz, ^1J(Rh–PPh) = 107 Hz, ^2J(PP) = 46 Hz (starting material));[12] (2) $\delta(PPh_2)$ 7.9, δ(PPh) 21.0 ($^1J(Rh-PPh_2)$ = 134 Hz, ^1J(Rh–PPh) = 160 Hz, ^2J(PP) = 55 Hz (marked by an asterisk in Figure 2)).

Spectrum 2 was observed to gradually decrease in intensity in favor of the resonance pattern of the starting compound, the spectral changes being accompanied by CO_2 evolution from the solution. We therefore assign the labeled signals of Figure 2 to a reversible CO_2 adduct Rh(4-MeC_6H_4)(bdpp)·CO_2 containing a loosely bound carbon dioxide ligand. Due to the ease with which the gas was released from this compound either in solution or in the solid state, attempts at purification and further characterization were unsuccessful. Significantly however, exposure of solutions of freshly prepared samples to the air induced the deposition of a yellow precipitate which, upon redissolution in pyridine, was easily identified as the peroxocarbonate 1 via ^{31}P NMR.

Acknowledgment. We gratefully acknowledge a generous gift of $RhCl_3{\cdot}xH_2O$ by DEGUSSA, Hanau. Thanks are also expressed to the staff of the X-ray laboratory of this institute for collecting diffraction data.

Registry No. 1, 89936-94-7; $Ir(CH_2SiMe_3)(CO)(PPh_3)_2$, 82180-73-2; $Ir(4\text{-}MeC_6H_4)(CO)(PPh_3)_2$, 59537-96-1; $Rh(CH_2SiMe_3)(CO)(PPh_3)_2$, 82180-77-6; $Rh(CH_2CMe_3)(CO)(PPh_3)_2$, 82180-78-7; $Rh(4\text{-}MeC_6H_4)(CO)(PPh_3)_2$, 82190-11-2; $Ir(CH_2SiMe_3)$(bdpp), 88492-99-3; Rh(4-MeC_6H_4)(bdpp), 84975-91-7; CO_2, 124-38-9.

Supplementary Material Available: A table of positional and thermal parameters and their estimated standard deviations and a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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[12] In ref 4a, the chemical shifts $\delta(PPh_2)$ and δ(PPh) of Rh(4-MeC_6H_4)(bdpp) have mistakenly been given as 19.3 and 3.3 ppm. Correct values are (at ca. 308 K) 16.3 and 0.3 ppm, respectively.

η^3-Allyl Complexes of Molybdenum: The Preparation and Structure of $[Mo(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$

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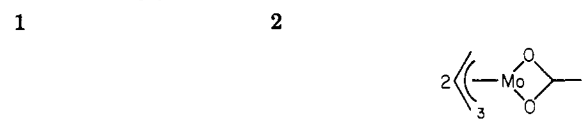
Summary: Tetra(η^3-allyl)molybdenum reacts with hydrogen chloride to give the tris(η^3-allyl)molybdenum chloride dimer. Further reaction with donor ligands causes monomerization while treatment with sodium cyclopentadienide leads to the formation of the paramagnetic complex $[Mo(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$ whose crystal structure has been determined by X-ray methods.

Although $[Mo(\eta^3\text{-}C_3H_5)_4]$ (1) has been known for 20 years,[1] supposed difficulties in its preparation have deterred a systematic investigation of its chemistry and it has even been suggested that it is relatively unreactive. We describe here an improved preparation and some representative reactions.

Addition of solid $MoCl_4{\cdot}2THF$ to a 20% excess of allylmagnesium chloride at room temperature in diethyl ether leads to the formation of 1 (ca. 40% yield)[2] as a sublimable, yellow solid without significant contamination from the green dimer $[Mo_2(\eta^3\text{-}C_3H_5)_4]$.

1 reacts quantitatively with HCl(g) at −70 °C in pentane and with iodine at −40 °C in diethyl ether with substitution of an allyl group by a halide to give $[MoCl(\eta^3\text{-}C_3H_5)_3]_2$ (2) as a pentane-insoluble pink solid stable below −30 °C and $[MoI(\eta^3\text{-}C_3H_5)_3]_2$ as a red-brown solid stable below −20 °C; both presumably as dimers. Treatment of the chloride with silver acetate leads to the formation of the pentane-soluble acetate 3 as a yellow solid that slowly decomposes at room temperature and melts with decomposition at 57 °C. The NMR spectra of 3 indicate the magnetic inequivalence of the three allyl groups.[3]



$$2[Mo(\eta^3\text{-}C_3H_5)_4] \xrightarrow[-2C_3H_6]{2HCl} [MoCl(\eta^3\text{-}C_3H_5)_3]_2 \xrightarrow[-2AgCl]{2AgOAc}$$

1 2 3

The chloride 2 and iodide have long been implied as the active species in the molybdenum-catalyzed polymerization of butadiene to give a polymer consisting almost exclusively of poly(1,2-butadiene),[4] and we have confirmed that they are indeed active at room temperature: 2 will even cause slow polymerization at −30 °C to give a polymer consisting of up to ca. 90% of poly(1,2-butadiene).

The chloride bridges in 2 can be cleaved by O, N, and P donor ligands, and the complexes $[MoCl(\eta^3\text{-}C_3H_5)_3L]$ (L = py, MeCN and PMe_3) have been isolated. Here again the NMR spectra indicate an asymmetric arrangement of the allyl groups. 2 can also be taken into solution by reaction with the Lewis acid $AlCl_3$ in toluene to give a violet solution from which it can be precipitated in crystalline form by addition of diethyl ether.

Treatment of 2 with sodium or thallium cyclopentadienide results in the formation of the orange, paramagnetic (1.44 μ_B) complex $[Mo(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$ (4). The monomeric nature of 4 in benzene solution is confirmed by a molecular weight determination (found 241

$$\underset{\mathbf{2}}{[MoCl(\eta^3\text{-}C_3H_5)_3]_2} + 2NaC_5H_5 \xrightarrow[-2C_3H_5\cdot]{-2NaCl} \underset{\mathbf{4}}{2[Mo(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]}$$

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(1) Oberkirch, W. Dissertation, Techn. Hochschule Aachen, 1963. Wilke, G.; Bogdanovič, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kröner, M.; Oberkirch, W.; Tanaka, K.; Steinrücke, E.; Walter, D.; Zimmermann, H. *Angew. Chem.* **1966,** *78,* 157. Cotton, F. A.; Pipal, J. R. *J. Am. Chem. Soc.* **1971,** *93,* 5441. Candlin, J. P.; Thomas, H. *Adv. Chem. Ser.* **1974,** *No. 132,* 212.

(2) Satisfactory analytical data have been obtained for all complexes reported here. The MS of 3 and 4 showed the parent ion M^+.

(3) ^1H NMR (400 MHz, −80 °C, CD_2Cl_2): δ 4.98, 4.56, 4.53 (m, meso-H); 3.62, 1.67, 0.90 (d, anti-H); 3.19, 1.19, 0.29 (d, anti-H); 3.56, 3.29, 3.03 (d, syn-H); 3.56, 3.04, 1.33 (d, syn-H). We thank R. Benn and A. Rufinska for the interpretation of this spectrum. All details of this and those of the other compounds reported here will be discussed in an extensive publication.

(4) Stroganov, V. S.; Novikova, E. S.; Frolov, V. M. *Kinet. Catal. (Engl. Transl.)* **1982,** *23,* 845. Novikova, E. S.; Stroganov, V. S.; Frolov, V. M. *Ibid.* **1981,** *22,* 1178 and references cited therein.

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