1212 (w), 1092 (m), 1045 (vs), 1020 (vs), 931 (w), 760 (w), 752 (w), 733 (m), 680 (s), 650 (s), 470 (m), 410 (m). ^{1}H NMR (−60 °C) δ 5.53, 4.58 (s, OCH_2-*t*-Bu), 4.21, 3.67 (d of an AB quartet, OCH_2-*t*-Bu), 3.82, 3.69 (d of an AB quartet, OCH_2-*t*-Bu), 3.32, 3.03 (s, Me_2NCN), 1.46, 1.14, 0.967, 0.870 (s, 1:1:2:2, OCH_2-*t*-Bu). Anal. Calcd: C, 50.50; H, 9.24; N, 3.57. Found: C, 50.44; H, 9.14; N, 3.46.

$Mo_2(OCH_2$-*t*-$Bu)_6(Et_2NCN)$. The diethylcyanamide complex was prepared in an analogous manner to that above but employing Et_2NCN: IR (cm^{-1}) 1552 (m), 1256 (w), 1210 (w), 1050 (sh), 1039 (s), 1012 (vs), 930 (w), 840 (w), 756 (m), 720 (m), 673 (m), 637 (m), 465 (m), ν(CN^{13}CN) 1522. ^{1}H NMR (−60 °C) 5.57, 4.64 (s, OCH_2-*t*-Bu), 4.25, 3.75, 3.86, 3.68 (d of AB quartets, OCH_2-*t*-Bu), 3.92, 3.55, 1.14 (q, mult, *Et*$_2$NCN), 1.65, 1.49, 0.998, 0.85 (s, 1:1:2:2, OCH_2-*t*-*Bu*). ^{13}C{^{1}H} NMR: δ 207 (Et_2NCN). Anal. Calcd: C, 51.72; H, 9.44; N, 3.45. Found: C, 51.47; H, 9.28, N, 3.53.

Computational Data. The model system $Mo_2(OH)_6(H_2NCN)$ was used to investigate the nature of the $M_2(R_2NCN)$ bonding. The coordinates were idealized to C_s symmetry, but otherwise bond lengths and angles were taken from the crystal structure of $Mo_2(OCH_2$-*t*-$Bu)_6(\mu$-$Me_2NCN)$. Nonempirical Hartree–Fock molecular orbital calculations were performed by H using the self-consistent field Fenske–Hall method (program MEDIEVEL). SCF calculations were performed in the atomic basis on H_2NCN (linear and bent) and $Mo_2(OH)_6$ fragments and on $Mo_2(OH)_6(\mu$-$H_2NCN)$. The converged wave functions for the fragments were transformed into appropriate fragment MO bases. Contour plots of the final molecular orbitals were generated via the programs MOPLOT and CONPLOT.

Basis functions for the atoms were generated by a best fit of Herman–Skillman atomic calculations. Contracted double-ζ representations were used for Mo 4d AO's as well as C, O, and N 2p AO's. The basis functions for the metal atoms were derived for a +1 oxidation state with the valence s and p exponents fixed at 1.8 for each of Mo 5s and 5p orbitals. An exponent of 1.16 was used for the H 1s atomic orbital.

Crystallographic Studies. General operating procedures and listings of programs have been previously given.[24] Crystal data are summarized in Table IV.

Data were collected at 165 °C; however, it was not possible to obtain a complete data set at this temperature due to a phase transition. A second data set was taken of the higher temperature phase. It appears the phase transition occurs near −120 °C. In any case there were no evidence of a transition during the present data collection. Attempts to lower the temperature to obtain the low-temperature phase were unsuccessful, with the crystal fracturing upon cooling.

The high-temperature phase was solved by Patterson and Fourier techniques, and all hydrogen atoms were located. Hydrogen thermal parameters were fixed and only their fractional coordinates allowed to vary during refinement. The primary difference is in the relative orientation of the OR groups, although a slight difference is seen in the $NCNMe_2$ ligand.

Acknowledgment. We thank the Department of Energy, Office of Basic Research, Chemical Sciences Division, and the Wrubel Computing Center for financial support and Professor David M. Hoffman for helpful and critical comments.

Registry No. $Mo_2(OCH_2$-*t*-$Bu)_6(Me_2NCN)$, 86784-87-4; $Mo_2(OCH_2$-*t*-$Bu)_6(Et_2NCN)$, 100813-13-6; $Mo_2(OH)_6(H_2NCN)$, 106905-66-2; $Et_2N^{13}CN$, 106905-67-3; $Mo_2(ONp)_6$, 62521-24-8; $Br^{13}CN$, 70610-98-9; Et_3N, 121-44-8; Mo, 7439-98-7.

Supplementary Material Available: Tables of anisotropic thermal parameters and complete listings of bond distances and angles (5 pages); listings of F_o and F_c (19 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of a Novel Rhodium(I) Complex, P_3RhP' ($P = P(OPh)_3$, $P' = PO(OPh)_2^-$): Application of 2D ^{31}P, ^{1}H, ^{13}C, and ^{17}O NMR Spectroscopy

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The structure of a novel rhodium(I) complex, P_3RhP' (1, $P = P(OPh)_3$, $P' = PO(OPh)_2^-$), was investigated by means of 2D ^{31}P, ^{13}C, ^{1}H, and ^{17}O NMR spectroscopy. The title compound may be prepared either via the reaction of $Rh(acac)(CO)_2$ with excess $P(OPh)_3$ in EtOH or by treating P_4RhClO_4 with KOH in $CHCl_3/C_6H_6$. In both cases a free or coordinated $P(OPh)_3$ ligand is transformed into a diphenyl phosphonate ion, $O{=}P(OPh)_2^-$, with concurrent loss of phenol. The mechanism of the resulting process may be interpreted as an organometallic variation on the Michaelis–Arbuzov reaction.

Introduction

Irreversible isomerization reactions with alkyl group migration in trialkyl phosphite ($P(OR)_3$) transition-metal complexes have been known for a long time.[1] $Ru(P(OCH_3)_3)_5$, for example, isomerizes already at 120 °C via a methyl group shift to form $((H_3CO)_3P)_4Ru(CH_3)P(O)(OCH_3)_2$.[2] Trimethyl phosphite undergoes isomerization at 200 °C to give $H_3CP(O)(OCH_3)_2$.[3] The process is catalyzed by methyl halides in the well-known Michaelis–Arbuzov reaction.[4] This kind of rearrangement or isomerization has hitherto not been observed for $P(OPh)_3$, whereas an

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extensive series of transition-metal complexes with ortho-coordinated $P(OPh)_3$ ligands has been characterized.[5]

In earlier studies we have reported on the synthesis and formation kinetics of $Rh(acac)P_2$[6,7] and on its reaction with excess $P(OPh)_3$ to form a complex that was first formulated as ortho-metalated $Rh(P(OPh)_3)_3(P(OPh)_2(OC_6H_4))$.[7] Recently it was reported that the ortho-metalated rhodium complex is also formed in the reaction of P_4RhClO_4 with KOH.[8] In our investigations of both reactions, which were carried out independently, we were unable to confirm this result. When no signals for possibly ortho-coordinated phenyl groups were observed in the 125.7-MHz ^{13}C NMR spectra, additional structural investigations were carried out. We were also able to obtain crystals suitable for X-ray diffraction, and preliminary measurements identified them as the square-planar Rh(I) complex 1.[9]

Experimental Section

All operations were carried out in argon atmosphere and with argon-saturated solvents.

Synthesis of P_3RhP'. (A) $Rh(acac)(CO)_2$ was prepared as described elsewhere.[10] $P(OPh)_3$ (480 mg, 1.55 mmol) was added dropwise to 100 mg (0.38 mmol) of $Rh(acac)(CO)_2$. After 10 min, 8 mL of argonated absolute ethanol was slowly introduced. The resulting precipitate of $Rh(acac)P_2$ was filtered off and the filtrate left to stand overnight. After about 5 h the wanted complex crystallized as thin yellow needles, mp 127 °C. Maximum yield was obtained with freshly distilled, argon-saturated $P(OPh)_3$ and EtOH. The first samples of this complex were prepared by Prof. J. J. Ziolkowski (University of Wroclaw).

(B) In the reaction of P_4RhClO_4 with KOH according to the procedure given in the literature,[8] we were unable to isolate the desired product. With altered reaction conditions the yield may be increased to 80%. ^{17}O-labeled 1 for ^{17}O NMR experiments was also obtained in this way. KOH (18 mg, 0.32 mmol) in 0.1 mL of $^{17}OH_2$ was added at room temperature with stirring to a solution of 100 mg (0.067 mmol) of P_4RhClO_4[11] in 4 mL of $CHCl_3/C_6H_6$ (4:1). The quickly formed white precipitate ($KClO_4$) was filtered off. After removal of solvent on a high vacuum line, one obtains ^{17}O-labeled P_3RhP' as a yellow powder, which exhibits spectroscopic data identical with those of the complex synthesized according to A.

Anal. Calcd for $RhP_4O_{12}C_{66}H_{55}{\cdot}C_2H_5OH$ (1312): C, 62.1; H, 4.6; P, 9.4; O, 15.8. Found: C, 61.4; H, 4.8; P, 8.9; O, 16.2. IR (cm^{-1}): 1576 s, 1476 s, 1270 w, 1187 vs, 1060 w, 1017 w, 1000 w, 900 vs, 700 s, 683 m, 605 w. Mass spectrum: *m/e* 310 ($P(OPh)_3^+$), 233 ($P(O)(OPh)_2^+$), 217 ($P(OPh)_2^+$), 154 (Ph_2^+), 94 ($PhOH^+$), and 77 (Ph^+). The molecular peak could not be observed due to the instability of the P_3RhP' complex, while the *m/e* 233 peak was obtained with high intensity. 2D ^{31}P (121.5 MHz), ^1H (300 MHz), and ^{13}C (125.7 MHz) NMR spectra were recorded on Bruker AM 300 and AM 500 spectrometers and with an Aspect 3000 computer. Mass spectra were obtained on a Varian CH7 spectrometer.

Results and Discussion

A number of spectroscopic investigations were carried out in an effort to identify the P_3RhP' species.

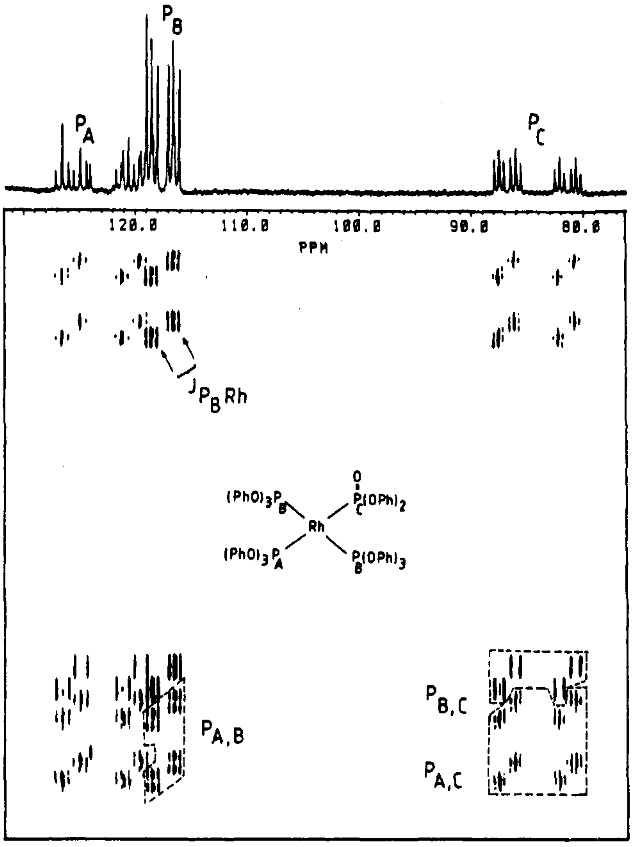

Figure 1. 121.5-MHz ^{31}P, ^{31}P COSY spectrum of P_3RhP' in $CDCl_3$ (pulse sequence 90°–t_1–90° FID; relaxation delay 2 s; 16 scan/increment; 128 FID's of 4K data points (followed by single zero filling in f_1 dimension); acquisition time 0.3 s). The three phosphorus–phosphorus cross peaks and one characteristic rhodium–phosphorus coupling $J_{Rh,B}$ are labeled in the spectrum. (Chemical shifts are relative to H_3PO_4 as external standard.)

The one-dimensional ^{31}P NMR spectrum of 1 recorded in argon-saturated $CDCl_3$ shows a false signal intensity ratio because of higher order and roof effects, and the peaks partially overlap. For technical reasons, we were unable to perform ^{31}P, ^{31}P decoupling. Therefore, for definite spectral assignment, we used a 2D ^{31}P NMR technique. The 2D ^{31}P, ^{31}P COSY spectrum (Figure 1) shows what is undoubtedly an AB_2C spin system with AB, AC, and BC cross terms of mutually coupling phosphorus nuclei, which are split by Rh–P coupling, as are all of the diagonal signals. All Rh–P couplings show the same relative signs. The spectrum was assigned on the basis of phosphite and phosphonate chemical shift patterns as well as on that of phosphorus–phosphorus coupling constants.[12] The coupling constants given below were confirmed by a computer simulation.[13]

P_A appears as a doublet of doublets of triplets at 124.5 ppm ($J(Rh–P_A)$ = 194.0 Hz, $^2J(P_B–P_A)$ = 69.6 Hz, $^2J(P_C–P_A)$ = −659 Hz), P_B as a doublet of doublets at 116.5 ppm ($J(Rh–P_B)$ = 242.5 Hz, $^2J(P_C–P_B)$ = 53.0 Hz, $^2J(P_A–P_B)$ = 69.6 Hz), and P_C again as a doublet of doublets of triplets at 82.3 ppm ($J(Rh–P_C)$ = 174.0 Hz, $^2J(P_A–P_C)$ = −659 Hz, $^2J(P_B–P_C)$ = 53.0 Hz). The phosphorus–phosphorus couplings indicate that two of the ligands are equivalent (P_B) and that the other two nonequivalent ligands occupy trans positions relative to one another: the larger P–P couplings of 659 Hz are due to the well-known trans effect,[14] while small couplings of 50–70 Hz point to

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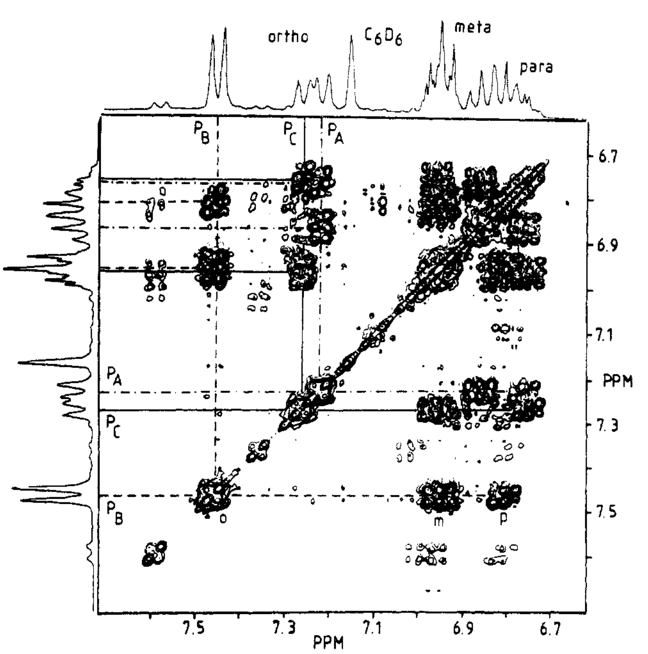

Figure 2. 300-MHz ^{1}H, ^{1}H COSY spectrum of P_3RhP' in the aromatic region (C_6D_6 solution; four scans/increment; 128 FID's of 512 data points; single zero filling). For the P_B group, ortho, meta, and para signals are obtained by following away from the diagonal along the lines shown (---). P_A and P_C group ortho, meta, and para protons are obtained by moving the lines labeled (—) and (-•-).

phosphorus nuclei in the cis configuration. An X-ray structure analysis[9] confirmed the positions of the phosphorus atoms: two of the phosphite ligands are found to have identical Rh–P_B distances of 226 pm, with the third one (P_A) in the trans position insignificantly smaller at 224 pm, while the phosphonate ligand, as expected,[15] exhibits a substantially increased Rh–P bond distance of 256 pm.

The ^{31}P spectra obtained at room temperature were not substantially changed upon cooling to 263 K. However, a number of higher order effects may be observed at this temperature.

2D ^{1}H NMR Spectra. The aromatic proton range of 1 in argon-saturated C_6D_6 is shown in Figure 2. The phenyl signals of the $P(OPh)_3$ and $O{=}P(OPh)_2^-$ ligands, overlapping in the one-dimensional ^{1}H NMR spectra, may be separated in the 2D COSY spectrum. As expected, three multiplets are observed for the ortho, meta, and para protons of the $P(OPh)_3$ groups. For the two symmetric phosphite ligands (P_B), the signals for the ortho protons appear at 7.45 ppm, split into a doublet by the meta protons, those for the meta protons appear as a triplet (doublet of doublet) at 6.94 ppm, and those of the para protons are present as a triplet at 6.8 ppm (Figure 2 (---)). The same type of coupling is observed for the nonsymmetrical phosphite (P_A) and phosphonate (P_C) ligand (P_A, 7.26 (ortho, d), 6.95 (meta, t), 6.75 ppm (para, t), P_C, 7.21 (ortho, d), 6.85 (meta, t), 6.74 ppm (para, t), cf. Figure 2 (—) and (-•-). For the nonoverlapping ortho proton signals, the ratio of the P_B:P_A:P_C intensities is 2:0.7:1 as expected.

^{13}C NMR Spectra. The 125.7-MHz broad-band-decoupled ^{13}C spectra of P_3RhP' (1) and P_4RhClO_4 in argon-saturated $CDCl_3$ are compared with each other in Figure 3. For the square-planar complex P_4RhClO_4, the ^{13}C signals of four different types of carbon atoms are observed as four singlets: ipso carbons at 150.9 ppm with low intensity due to the NOE effect; meta, ortho, and para carbons at 129.84, 125.5, and 120.0 ppm, respectively. The phosphorus–carbon couplings expected for ipso and ortho carbons are not observed, and are probably smaller than 1 Hz.[16] This was also observed for closely related rhodium–triphenyl phosphite complexes (Table I). For complex 1, the AB_2C-type spin system assigned in the ^{31}P spectra is also observed in ^{13}C NMR. Three different ipso carbon signals appear. The first is a set of averaged doublets at 153.1 ppm ($^2J_{C-P}$ = 14.8 Hz, P_C carbons), the second is a broad singlet at 151.6 ppm (P_B), and the third is again an averaged set of doublets ($^2J_{C-P}$ = 8.6 Hz, P_A carbons). This assignment may also be arrived at via comparison of the phosphorus–carbon coupling in P_3RhP' with the complexes P_2RhP' $(CO)_2$[17] and P_3RhCl (Table I). For the meta carbons, three separate signals are observed at 129.3 (P_A carbons), 129.2 (P_B carbons), and 128.3 ppm (P_C carbons), while for the para only two signals are obtained at 124.2 and 123.9 ppm. Two of the para signals may possibly overlap. However, in a Me_2SO-d_6/$CDCl_3$

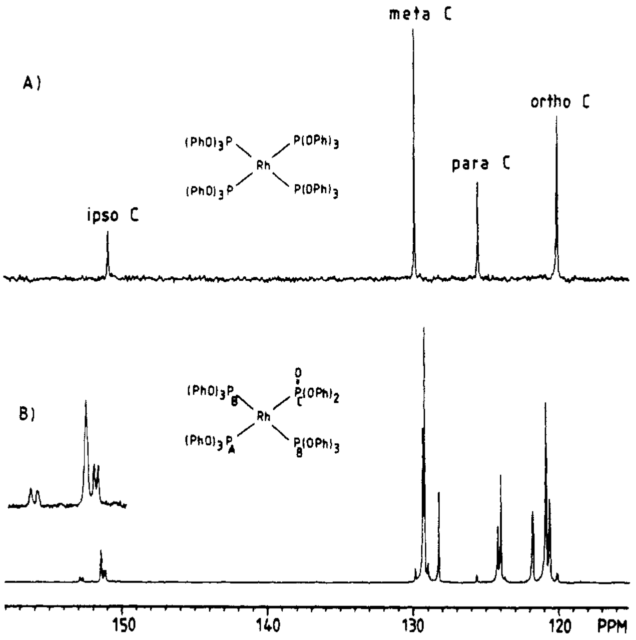

Figure 3. 125.7-MHz ^{1}H broad-band-decoupled ^{13}C NMR spectra of P_4RhClO_4 (A) and P_3RhP' (B) in the aromatic region ($CDCl_3$ solution).

Table I. ^{13}C NMR Data of Different Phosphite and Phosphonate Compounds ($P = P(OPh)_3$, $P' = P(O)(OPh)_2^-$)

	$\delta_{ipso\text{-}C}$ ($^2J_{CP}$, Hz)	$\delta_{meta\text{-}C}$	$\delta_{para\text{-}C}$	$\delta_{ortho\text{-}C}$ ($^3J_{CP}$, Hz)
$P(OPh)_3$	151.5 (3.36)	129.64	124.18	120.65 (7.0)
$O{=}P(OPh)_3$	150.4 (8.0)	129.7	125.6	120.0 (4.8)
$O{=}PH(OPh)_2$	148.81 (8.15)	129.7	125.5	120.12 (4.9)
RhP_4ClO_4	150.9	129.84	125.5	120.0
$HRhP_4$	152.36	128.97	123.2	121.64
$(acac)RhP_2$	152.35	128.90	123.7	120,9
P_3RhCl	151.6 (6.3)	129.14	124.12	120.8 (5.8)
	151.38	128.77	124.01	120.2
$P_2RhP'(CO)_2$	152.2 (10.6, P′)	129.7	125.1	121.6
	151.0 (P)	128.9	123.3	121.4 (4.4)
$HRhP_3CO$	151.72	128.92	123.66	121.64

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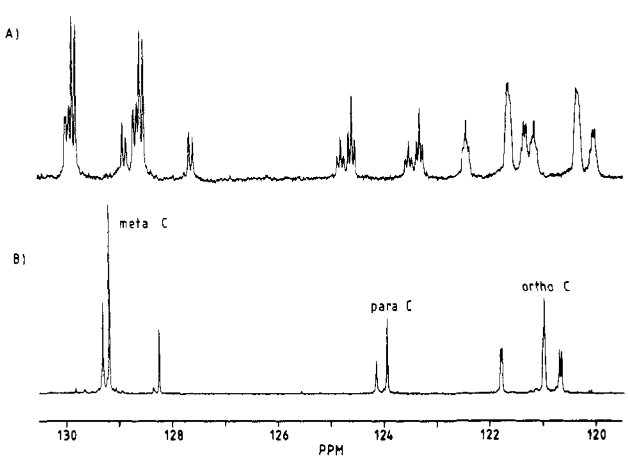

Figure 4. 125.7-MHz ^1H off-resonance-decoupled (A) and ^1H broad-band-decoupled (B) ^{13}C NMR spectra of P_3RhP' in the aromatic region ($CDCl_3$ solution).

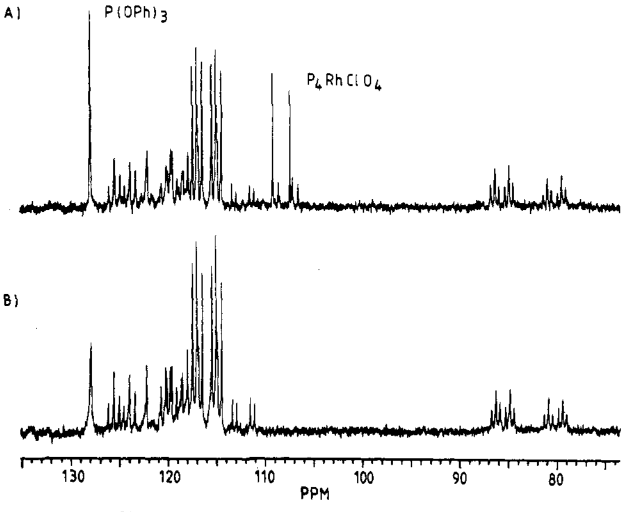

Figure 5. ^{31}P NMR spectra at 121.5 MHz for the reaction $P_4RhClO_4 \xrightarrow{K^{17}OH} P_3RhP'$: (A) after 25 min; (B) after 60 min.

(7:3) solvent mixture, the ^{13}C NMR spectrum of 1 does exhibit a third signal for the para carbons. Unfortunately, in this medium the ipso carbons are not very well-resolved. The ortho carbons appear as three separate signals. One at 121.7 ppm is an unresolved doublet for the P_C carbons, one at 120.9 ppm appears as a broad singlet for the P_B carbons, and one at 120.6 ppm is again an averaged set of doublets ($^3J_{C-P}$ = 5.0 Hz) for the P_A carbons. In the off-resonance-decoupled ^{13}C spectrum, the above assignment of ortho, meta, and para carbons is confirmed: meta carbons appear as a doublet of doublets, para carbons as a doublet of triplets, and ortho carbons as a doublet of multiplets (Figure 4).

^{17}O NMR Spectra and Mechanism of Formation of P_3RhP'. In order to elucidate the reaction mechanism for the formation of 1 from P_4RhClO_4 and $K^{17}OH$, the reaction mixture was investigated by means of ^{31}P and ^{17}O NMR spectroscopy (Figures 5 and 6). P_4RhClO_4 (50 mg) was dissolved in 3 mL of an argon-saturated $CDCl_3/C_6D_6$ mixture (4:1) and the ^{31}P NMR spectrum registered. The symmetric phosphite ligands appear as a doublet at 108 ppm (J_{Rh-P} = 220 Hz). After 9 mg of KOH in 0.1 mL of $^{17}OH_2$ was added and the mixture shaken vigorously, the precipitated $KClO_4$ was filtered off, and ^{31}P spectra were registered at different intervals (Figure 5). After 25 min, the ^{31}P spectrum shows at 108 ppm the peak of the precursor P_4RhClO_4, at 128 ppm the free $P(OPh)_3$ ligand, and the new signals due to the P_3RhP' complex (see above).

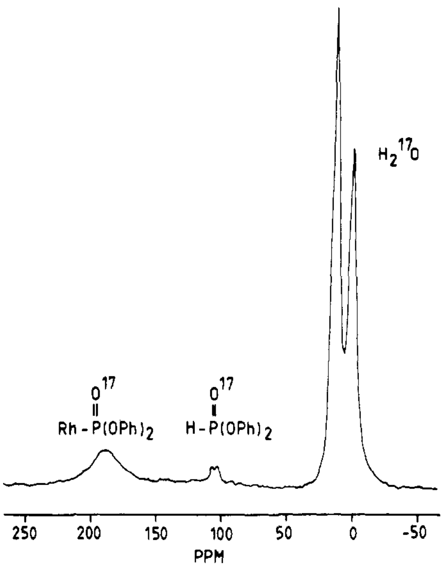

Figure 6. 40.5-MHz ^{17}O NMR spectrum of the reaction $P_4RhClO_4 \xrightarrow{K^{17}OH} P_3RhP'$ after 70 min.

After 60 min, the precursor signals have vanished completely and those of the free phosphite ligand have decreased in intensity, while the characteristic signals of the P_3RhP' complex 1 have reached full intensity (Figure 5, cf. also Figure 1). In the ^1H NMR spectra intense phenol signals are observed. The ^{17}O NMR spectrum of the same sample (vs. externally calibrated $H_2{}^{17}O$ signal at 0 ppm) exhibits a doublet at 104 ppm (J_{O-P} = 170 Hz), a multiplet at 190 ppm, and two $H_2{}^{17}O$ signals at 13 and 3 ppm. An upfield shifted $H_2{}^{17}O$ signal at 13 ppm may result from an interaction of $H_2{}^{17}O$ with complex 1 (Figure 6).[18] Since the latter may possibly derive from partial oxygen exchange of $P(OPh)_3$ in $K^{17}OH$ solution, a further experiment with 100 mg of $P(OPh)_3$ in 0.1 mL of $H_2{}^{17}O$ was carried out for comparison purposes. The ^{17}O NMR spectrum of the sample showed a well-resolved doublet at 114.6 ppm (J_{P-O} = 168 Hz) and the ^{31}P spectrum a doublet at -0.9 ppm with J_{P-H} = 740 Hz, which is assigned to the known[19] spectrum of the diphenyl ester of phosphorous acid, $O{=}PH(OPh)_2$. The ^{17}O-labeled complex 1, isolated in pure form, exhibits a multiplet at 188 ppm, which is assigned to the coordinated $^{17}O{=}P(OPh)_2^-$ ligand, the signals of which are broadened by unresolved P–O and Rh–P couplings; in contrast, a doublet structure resulting from P–O coupling is easily observed for the free $^{17}O{=}PH(OPh)_2$ species. The chemical shifts and phosphorus–oxygen couplings compare well with literature values.[20] The above investigations illustrate the usefulness of ^{17}O NMR spectroscopy in structure assignments of ^{17}O labeled complexes. The stability of the P_3RhP' complex was moreover investigated with ^1H and ^{31}P NMR spectroscopy. In non-argon-saturated solution, decomposition occurs within 1 day, with triphenyl phosphate, $O{=}P(OPh)_3$, being the only observable product. In argon-saturated solution, the complex is comparatively stable, with only slight decomposition being observed after 4 weeks. The reactions of P_3RhP' with H_2 and CO will be reported shortly.[17]

Finally, we would like to make a few concluding remarks concerning the mechanism of the reported reactions. In the reaction of $Rh(acac)(CO)_2$ with four $P(OPh)_3$ in EtOH,

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the intermediate complex $P_4Rh^+(acac)^-$ is first formed and slowly rearranges into the less soluble P_3Rh^+–$P(O)(OPh)_2^-$ species. The formation of the P_4Rh^+ species was observed very clearly in the ^{31}P NMR spectrum. The rearrangement process is significantly faster (ca. 30 min at room temperature when P_4RhClO_4 is treated with KOH. A possible intermediate with either a directly or ortho coordinated phenyl group could not be observed, whereas the formation of phenol could be unambiguosly detected by ^1H NMR spectroscopy. The novel rearrangement of $P(OPh)_3$ to $O{=}P(OPh)_2^-$ in $CDCl_3/C_6D_6$ with KOH observed here lends support to the feasibility of such a reaction in the RhP_4^+ species. Thus the main structural elements of 1 in solution could be derived from extensive NMR spectroscopic investigations without resorting to X-ray structure analysis.

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(η^5-Tris(trimethylsilyl)cyclopentadienyl)magnesium Compounds: Syntheses and Structures

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The new compounds methyl(N,N,N',N'-tetramethylethylenediamine)(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium (A), bis(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium (B), and bromo(N,N,N',N'-tetramethylethylenediamine)(η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl)magnesium (C) have been prepared and characterized. The crystal and molecular structures of B and C have been determined by X-ray diffraction. B: $C_{28}H_{58}MgSi_6$, a = 18.794 (3) Å, b = 22.720 (4) Å, c = 19.803 (1) Å, β = 108.82 (1)°, space group $P2_1/a$ (No. 14), Z = 8, monoclinic, $F(000)$ = 2576; R = 0.087 for 5578 observed reflections. C: $C_{20}H_{45}BrMgN_2Si_3$, a = 9.546 (1) Å, b = 10.852 (1) Å, c = 30.727 (2) Å, α = 97.19 (1)°, β = 93.01 (1)°, γ = 110.41 (1)°, space group $P\bar{1}$ (No. 2), Z = 4, triclinic, $F(000)$ = 1076; R = 0.050 for 6096 observed reflections. The two cyclopentadienyl ligands in B are nonparallel, and the average Cp–Mg–Cp angle is 171.1°; this can be attributed to steric repulsion between the bulky trimethylsilyl substituents on the rings. Multinuclear NMR spectroscopy has been used to study the structure of A, B, and C in solution. Restricted rotation of the cyclopentadienyl rings in B is observed at low temperature.

Introduction

The ability of elements of groups IA and IIA (1 and 2[38]) to participate in polyhapto bonding with cyclopentadienyl ligands has received increasingly wide study in the past few years, particularly from a theoretical point of view.[1,2] Synthetic work has tended to concentrate on the organolithium compounds, and recently several structures of (η^5-cyclopentadienyl)lithium compounds have been published.[3] In comparison, the cyclopentadienyl chemistry of magnesium has been somewhat neglected, although the cyclopentadienyl Grignard reagent (C_5H_5MgBr) has been known for 70 years.[4]

Bis(η^5-cyclopentadienyl)magnesium ("magnesocene") was first prepared in 1954,[5] and arguments about the nature of the metal–ring bonding have continued sporadically ever since. Wilkinson, Cotton, and Birmingham originally proposed an ionic formulation for magnesocene on the basis of mass[6] and infrared spectral data, chemical properties, and its electrical conductance in liquid ammonia solution.[7] Lippincott et al.[8] disagreed with this and published infrared data supporting their suggestion that magnesocene should be considered as an essentially covalent compound. The reliability of these data has, how-

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