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Crystal Structure of the Cis Hydride Acetyl Complex $[\{N(CH_2CH_2PPh_2)_3\}Rh(H)(COMe)]BPh_4$. One-Pot Synthesis of ($\sigma$-Acyl)metal Complexes from Aldehydes

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Summary: The first crystal structure of a *cis*-hydridoacylmetal complex, namely $[(NP_3)Rh(H)(COMe)]BPh_4$ (**1**), has been determined by X-ray methods (NP_3 = $N(CH_2CH_2PPh_2)_3$). The Rh center is coordinated by the four donor atoms of NP_3 and by mutually cis-disposed hydride and acetyl ligands in a distorted-octahedral geometry. Complex **1** in THF reacts with $NaBH_4$ to give the Rh(I) σ-acetyl $[(NP_3)Rh(COMe)]$, which in turn converts to **1** by treatment with triflic acid. Reaction of the hydride formyl complex $[(NP_3)Rh(H)(CHO)]BPh_4$ with $NaBH_4$ yields the hydride carbonyl $[(NP_3)Rh(H)(CO)]$.

In a previous paper we showed that the 16-electron fragment $[(NP_3)Rh]^+$ is able to activate C–H bonds from aldehydes, forming stable *cis*-hydridoacylrhodium(III) complexes of the type $[(NP_3)Rh(H)(COR)]BPh_4$ (NP_3 = $N(CH_2CH_2PPh_2)_3$; R = H, alkyl, aryl).[1] On the basis of IR and NMR data, these compounds were assigned an octahedral (OCT) structure where the hydride ligand stereospecifically lies trans to a terminal phosphorus of the tripodal ligand (Scheme I).

Since no crystal structure for hydridoacyl metal complexes has been reported in the literature,[2] we decided to grow crystals of some of our NP_3 derivatives that would be suitable for an X-ray analysis. We have been successful with the acetyl $[(NP_3)Rh(H)(COMe)]BPh_4$ (1), whose crystal structure is herein described together with a new, simple route to (σ-acyl)metal complexes.

Experimental Section

General Data. Tetrahydrofuran (THF) and acetone were purified by distillation over $LiAlH_4$ and P_2O_5 under nitrogen just prior to use, respectively. All the other solvents and chemicals employed were reagent grade and were used as received. The compounds $[(NP_3)Rh(H)(COMe)]BPh_4$ (1),[1] $[(NP_3)Rh(H)(CHO)]BPh_4$ (4),[1] and $[(NP_3)Rh(CO)]BPh_4$ (6)[3] were prepared according to published procedures. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. ^1H NMR spectra were recorded at 299.945 MHz on a Varian VXR 300 spectrometer. Peak positions are relative to tetramethylsilane as external reference. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian VXR 300 instrument operating at 121.42 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive.

Synthesis of the Complexes. All reactions and manipulations were routinely performed under a nitrogen atmosphere by using Schlenk-line techniques. The solid compounds were collected on sintered-glass frits and washed with ethanol and light petroleum ether (bp 50-70 °C) before being dried under a stream of nitrogen.

The preparations and principal reactions of the complexes described in this paper are summarized in Scheme I.

Preparation of $[(NP_3)Rh(COMe)]$ (2). A solution of $NaBH_4$ (0.08 g, 2.10 mmol) in ethanol (25 mL) was added portionwise over 5 min to a solution of 1 (0.75 g, 0.67 mmol) in THF (50 mL). The mixture was heated to reflux temperature and then stirred for 6 h. Addition of ethanol to the reaction mixture, cooled to room temperature, and slow evaporation of the solvents gave yellow crystals of 2, yield 80%. Anal. Calcd for $C_{44}H_{45}NOP_3Rh$: C, 66.09; H, 5.67; N, 1.75; Rh, 12.87. Found: C, 65.94; H, 5.61; N, 1.60; Rh, 12.74.

Preparation of $[(NP_3)Rh(H)(CO)]$ (5). Method A. The hydride carbonyl complex 5 was obtained as yellow crystals in ca. 75% yield by replacing 1 with 4 in the above procedure. Anal. Calcd for $C_{43}H_{43}NOP_3Rh$: C, 65.74; H, 5.52; N, 1.78; Rh, 13.10. Found: C, 65.69; H, 5.55; N, 1.71; Rh, 12.94.

Method B. Solid $NaBH_4$ (0.08 g, 2.10 mmol) was added to a THF (60 mL) solution of $[(NP_3)Rh(CO)]BPh_4$ (6; 0.80 g, 0.74 mmol) with vigorous stirring. On addition of ethanol (50 mL) and slow evaporation of the solvents at room temperature, yellow crystals of 5 were obtained in 85% yield.

Reaction of 2 with $HOSO_2CF_3$. Neat triflic acid (60 μL, 0.68 mmol) was syringed into a THF solution (50 mL) of 2 (0.48 g, 0.60 mmol). The solution immediately turned colorless. Addition of $NaBPh_4$ (0.37 g, 1.08 mmol) and ethanol (40 mL) yielded white crystals of 1, yield 90%.

X-ray Crystallography. The X-ray analysis was undertaken on yellow crystals of $[(NP_3)Rh(H)(COMe)]BPh_4$ (1) grown by slow evaporation of a 2:1 acetone/ethanol solution. The crystals are monoclinic, space group $P2_1/n$. A prismatic crystal of 0.45 × 0.20 × 0.60 mm approximate dimensions was selected and used for the collection of data. The unit-cell dimensions were determined by a least-squares refinement of the setting angles of 15 angle reflections ($20 < 2\theta < 26°$) carefully centered. The intensities were collected on a Nicolet R3 computer-controlled diffractometer using graphite-monochromated Mo Kα radiation in the ω-scan mode at variable scan rate. Three standards were measured every 100 reflections and were found to remain constant. All the reflections were processed to yield values of I and $\sigma(I)$;[4] in the estimation of $\sigma(I)$ the uncertainty factor p = 0.007 was calculated from the variance of the standard reflections.[5] Corrections for Lorentz and polarization were applied. An empirical absorption correction[6] was applied with use of φ-scan data of three reflections at χ angles of 91.1°. The minimum normalized transmission factors were in the range 0.70–0.74. Only the independent reflections that met the conditions $I > 3\sigma(I)$ were used in the subsequent calculations. In Table I the crystallographic data are summarized.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures with the minimized

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[1] Bianchini, C.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Vizza, F.; Zanobini, F. *Organometallics* **1989**, *8*, 337.

[2] See for example: (a) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221. (b) Thorn, D. L.; Roe, D. C. *Organometallics* **1987**, *6*, 617. (c) Bruno, J. W.; Fermin, M. C.; Halfan, S. E.; Schulte, G. K. *J. Am. Chem. Soc.* **1989**, *111*, 8738. (d) Landvatter, E. F.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 506.

[3] Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411.

[4] Bachechi, F.; Zambonelli, L.; Marcotrigiano, G. *J. Cryst. Mol. Struct.* **1977**, *7*, 11.

[5] McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr.* **1975**, *A31*, 245.

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

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Scheme I

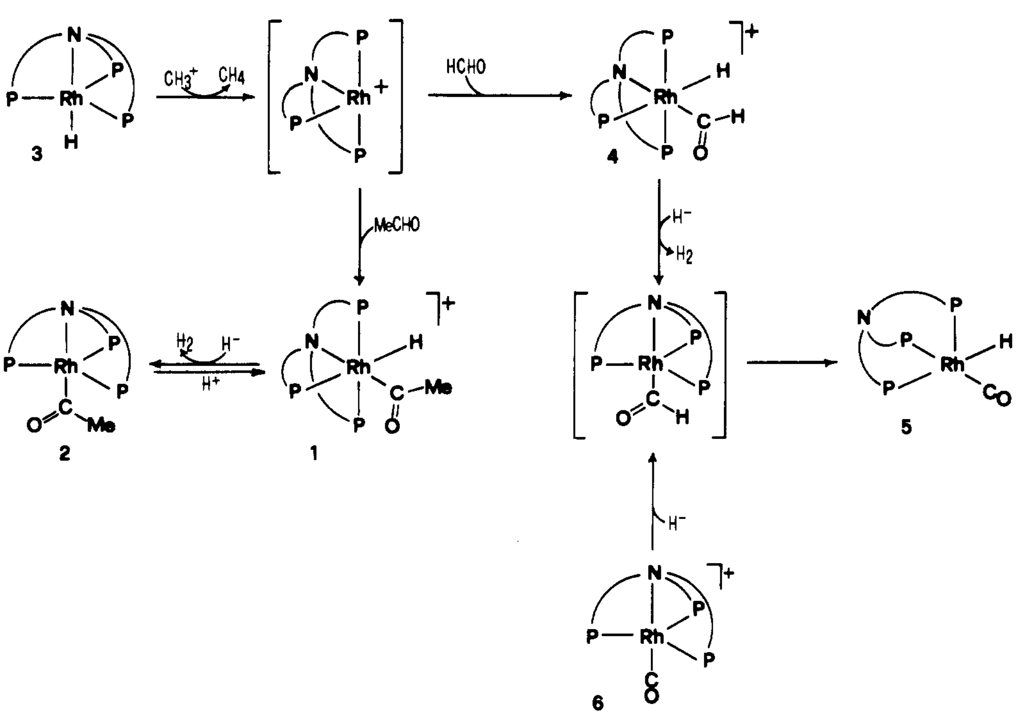

Table I. X-ray Diffraction Data

formula	$C_{68}H_{66}BNOP_3Rh$
mol wt	1119.9
a, Å	18.464 (6)
b, Å	15.522 (7)
c, Å	19.634 (6)
β, deg	94.69 (3)
V, Å^3	5608.4
Z	4
cryst syst	monoclinic
space group	$P2_1/n$
calcd density, g cm^{-3}	1.326
cryst dimens, mm	0.45 × 0.20 × 0.60
radiation	graphite-monochromated Mo Kα (λ = 0.71069 Å)
abs coeff, cm^{-1}	4.26
scan mode	ω scan
scan range, deg	0.8
scan speed	variable according to intens
bkgd counts	0.5 scan time at +0.8
intensity control stds	3 measd every 100 rflns
2θ angle, deg	3–56
total no. of observns	10861
no. of unique data with $I > 3\sigma(I)$	3298
data/param ratio	5
no. of params refined	676
R	0.054
R_w	0.067

function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. After convergence of the isotropic refinement at R = 0.079, all the hydrogen atoms bound to carbon atoms were introduced into calculated positions (C–H = 0.96 Å) and refined riding on the corresponding carbon atoms. All the hydrogen atoms were given the isotropic thermal factors of the parent carbon atoms and were not refined. The hydride ligand could not be unambiguously located on the difference Fourier maps calculated with low sin θ reflections at the last stages of the refinement and was not included in the calculations. The final cycles of refinements converged at R = 0.054 and R_w = 0.067. The final Fourier map did not reveal significant peaks. All calculations were performed on the Data General Eclipse MV8000II computer using local programs. Scattering factors and anomalous dispersion terms were taken from ref 7.

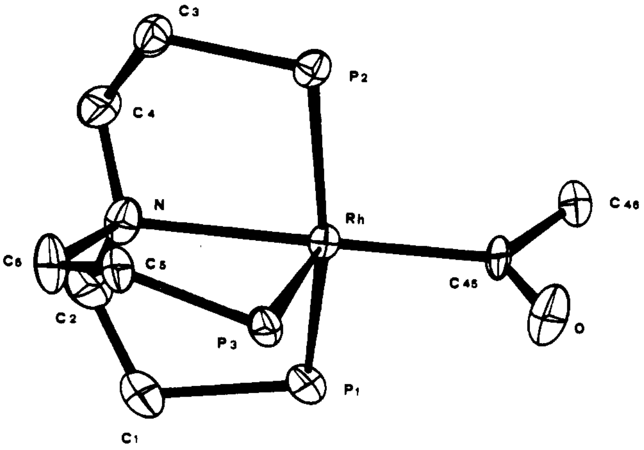

Figure 1. Inner coordination sphere of the cationic complex $[(NP_3)Rh(H)(COCH_3)]^+$. The ellipsoids represent 30% probability.

Final atomic parameters of the non-hydrogen atoms are given in Table II.

Results and Discussion

The crystal structure of 1 consists of discrete $[(NP_3)Rh(H)(COMe)]^+$ cations and $[BPh_4]^-$ anions with no short contacts between atoms of different ions.

A perspective view of the core of the cationic complex is shown in Figure 1 and Table III lists a selection of intramolecular distances and angles with their standard deviations.

The Rh atom is hexacoordinated by the bridgehead nitrogen atom and by the three phosphorus atoms of the NP_3 ligand, by C(45) of the acetyl group, and by the hydride ligand. The hydride ligand was not located in the difference Fourier maps, but its presence in the solid is based on spectroscopic data and its position can be inferred from the arrangement of the heavier atoms. In good accord with the ^{31}P and ^1H NMR data, the acetyl group lies trans to the nitrogen atom and cis to the site of the hydride ligand. The coordination geometry around the Rh atom

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(7) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table II. Atomic Coordinates with Their Esd's in Parentheses

	x	*y*	*z*
Rh	0.1753 (1)	0.1935 (1)	0.38001 (5)
P(1)	0.0530 (2)	0.1906 (2)	0.3450 (1)
P(2)	0.2807 (2)	0.1840 (2)	0.4509 (2)
P(3)	0.2012 (2)	0.3202 (2)	0.3149 (2)
N	0.1403 (6)	0.2929 (6)	0.4588 (5)
O	0.2415 (6)	0.1154 (6)	0.2693 (5)
B	−0.2159 (9)	0.3758 (9)	0.4041 (7)
C(1)	0.0141 (8)	0.2646 (9)	0.4076 (7)
C(2)	0.0652 (7)	0.2734 (8)	0.4710 (7)
C(3)	0.2683 (9)	0.2745 (9)	0.5104 (8)
C(4)	0.1892 (9)	0.2821 (9)	0.5229 (8)
C(5)	0.1435 (8)	0.3957 (8)	0.3560 (6)
C(6)	0.147 (1)	0.3867 (7)	0.4337 (7)
C(7)	0.0203 (7)	0.2299 (7)	0.2608 (6)
C(8)	0.0498 (6)	0.1913 (9)	0.2046 (6)
C(9)	0.0228 (9)	0.215 (1)	0.1395 (7)
C(10)	−0.0298 (8)	0.276 (1)	0.1299 (8)
C(11)	−0.0590 (9)	0.316 (1)	0.1842 (8)
C(12)	−0.0325 (7)	0.2936 (9)	0.2507 (8)
C(13)	0.0014 (7)	0.0905 (8)	0.3497 (6)
C(14)	−0.0518 (9)	0.066 (1)	0.3004 (9)
C(15)	−0.089 (1)	−0.012 (1)	0.305 (1)
C(16)	−0.073 (1)	−0.067 (1)	0.3572 (9)
C(17)	−0.0197 (9)	−0.0457 (9)	0.406 (1)
C(18)	0.017 (1)	0.031 (1)	0.4028 (9)
C(19)	0.2935 (8)	0.0908 (8)	0.5073 (6)
C(20)	0.3610 (9)	0.0605 (9)	0.5285 (7)
C(21)	0.369 (1)	−0.008 (1)	0.5729 (8)
C(22)	0.313 (1)	−0.0450 (9)	0.5984 (8)
C(23)	0.243 (1)	−0.018 (1)	0.580 (1)
C(24)	0.2328 (9)	0.052 (1)	0.5347 (8)
C(25)	0.3717 (6)	0.1992 (8)	0.4222 (6)
C(26)	0.393 (1)	0.1406 (9)	0.3723 (9)
C(27)	0.465 (1)	0.143 (1)	0.354 (1)
C(28)	0.5113 (8)	0.204 (1)	0.382 (1)
C(29)	0.489 (1)	0.257 (1)	0.429 (1)
C(30)	0.4213 (8)	0.259 (1)	0.4497 (8)
C(31)	0.1764 (7)	0.3335 (7)	0.2231 (6)
C(32)	0.2070 (8)	0.2804 (8)	0.1767 (7)
C(33)	0.1937 (8)	0.295 (1)	0.1059 (7)
C(34)	0.149 (1)	0.358 (1)	0.0834 (9)
C(35)	0.116 (1)	0.409 (1)	0.1263 (8)
C(36)	0.1320 (9)	0.4001 (7)	0.1978 (7)
C(37)	0.2919 (7)	0.3670 (8)	0.3201 (7)
C(38)	0.308 (1)	0.445 (1)	0.3544 (7)
C(39)	0.378 (1)	0.479 (1)	0.353 (1)
C(40)	0.431 (1)	0.439 (1)	0.3220 (9)
C(41)	0.4143 (9)	0.362 (1)	0.2891 (9)
C(42)	0.3468 (7)	0.3255 (8)	0.2895 (6)
C(45)	0.2072 (6)	0.1017 (7)	0.3187 (5)
C(46)	0.1916 (9)	0.0086 (8)	0.3348 (8)
C(50)	−0.2505 (7)	0.3113 (9)	0.3414 (6)
C(51)	−0.2059 (9)	0.2532 (9)	0.3125 (8)
C(52)	−0.230 (1)	0.202 (1)	0.2562 (8)
C(53)	−0.302 (1)	0.203 (1)	0.2315 (8)
C(54)	−0.3480 (9)	0.258 (1)	0.2609 (8)
C(55)	−0.3228 (7)	0.3111 (9)	0.3161 (6)
C(56)	−0.1491 (7)	0.4319 (8)	0.3762 (7)
C(57)	−0.1497 (7)	0.4592 (9)	0.3062 (7)
C(58)	−0.0971 (8)	0.5097 (9)	0.2821 (8)
C(59)	−0.0388 (8)	0.538 (1)	0.3258 (9)
C(60)	−0.0359 (8)	0.5132 (9)	0.3936 (8)
C(61)	−0.0903 (8)	0.4602 (9)	0.4172 (7)
C(62)	−0.1856 (7)	0.3237 (8)	0.4717 (6)
C(63)	−0.1700 (9)	0.2360 (8)	0.4733 (8)
C(64)	−0.138 (1)	0.197 (1)	0.532 (1)
C(65)	−0.122 (1)	0.239 (2)	0.591 (1)
C(66)	−0.140 (1)	0.325 (1)	0.5926 (8)
C(67)	−0.1728 (9)	0.365 (1)	0.5345 (8)
C(68)	−0.2830 (7)	0.4434 (7)	0.4210 (6)
C(69)	−0.2980 (7)	0.5202 (9)	0.3852 (7)
C(70)	−0.3609 (8)	0.5694 (9)	0.3924 (8)
C(71)	−0.4095 (8)	0.5397 (9)	0.4350 (8)
C(72)	−0.3972 (9)	0.465 (1)	0.4725 (7)
C(73)	−0.3354 (9)	0.419 (1)	0.4633 (8)

Table III. Selected Bond Distances (Å) and Angles (deg)

Rh–P(1)	2.305 (3)	P(3)–C(5)	1.82 (1)
Rh–P(2)	2.303 (3)	P(3)–C(31)	1.83 (1)
Rh–P(3)	2.414 (3)	P(3)–C(37)	1.82 (1)
Rh–N	2.31 (1)	N–C(2)	1.46 (2)
Rh–C(45)	1.99 (1)	N–C(4)	1.50 (2)
P(1)–C(1)	1.87 (1)	N–C(6)	1.54 (2)
P(1)–C(7)	1.82 (1)	O–C(45)	1.22 (1)
P(1)–C(13)	1.83 (1)	C(45)–C(46)	1.51 (2)
P(2)–C(3)	1.85 (1)	C(1)–C(2)	1.51 (2)
P(2)–C(19)	1.82 (1)	C(3)–C(4)	1.50 (2)
P(2)–C(25)	1.83 (1)	C(5)–C(6)	1.53 (2)
P(2)–Rh–P(1)	159.6 (1)	C(25)–P(2)–C(3)	105.1 (7)
P(3)–Rh–P(1)	95.1 (1)	C(25)–P(2)–C(19)	102.2 (6)
P(3)–Rh–P(2)	100.2 (1)	C(5)–P(3)–Rh	98.1 (4)
N–Rh–P(1)	83.8 (3)	C(31)–P(3)–Rh	124.6 (4)
N–Rh–P(2)	84.7 (3)	C(37)–P(3)–Rh	121.1 (4)
N–Rh–P(3)	83.6 (3)	C(31)–P(3)–C(5)	104.8 (6)
C(45)–Rh–P(1)	97.9 (4)	C(37)–P(3)–C(5)	106.8 (6)
C(45)–Rh–P(2)	92.5 (4)	C(37)–P(3)–C(31)	99.4 (6)
C(45)–Rh–P(3)	100.5 (3)	O–C(45)–Rh	123.8 (8)
C(45)–Rh–N	175.4 (4)	C(46)–C(45)–Rh	119.2 (9)
C(1)–P(1)–Rh	102.3 (5)	C(46)–C(45)–O	117 (1)
C(7)–P(1)–Rh	120.6 (4)	C(4)–N–C(2)	111 (1)
C(13)–P(1)–Rh	120.2 (5)	C(6)–N–C(2)	110 (1)
C(7)–P(1)–C(1)	105.9 (6)	C(6)–N–C(4)	108 (1)
C(13)–P(1)–C(1)	105.0 (6)	C(2)–C(1)–P(1)	110 (1)
C(13)–P(1)–C(7)	101.2 (6)	C(1)–C(2)–N	115 (1)
C(3)–P(2)–Rh	101.0 (5)	C(4)–C(3)–P(2)	110 (1)
C(19)–P(2)–Rh	118.6 (5)	C(3)–C(4)–N	113 (1)
C(25)–P(2)–Rh	123.8 (4)	C(6)–C(5)–P(3)	114 (1)
C(19)–P(2)–C(3)	103.6 (6)	C(5)–C(6)–N	114 (1)

is distorted-octahedral and is characterized by the butterfly shape that the [(NP$_3$)Rh] moiety assumes in octahedral complexes of the NP$_3$ ligand.[3,8] The three P–Rh–N angles (83.6 (4), 85.0 (4), 83.8 (3)°) are smaller than the ideal values, and the mutually trans P(1) and P(2) are bent toward the site of the hydride ligand with a bond angle of 159.6 (1)°. The Rh–P(1) and Rh–P(2) bond lengths are equivalent (average 2.303 Å) and are in the expected range for alkylarylphosphine–Rh distances, while Rh–P(3) (2.416 (4) Å) is much longer and seems to reflect a trans influence, exerted by the hydride ligand, stronger than in analogous hydrido complexes.[8,9] The acetyl group lies in the plane defined by Rh, N, and P(3) and presents a geometry (C(45)–O = 1.23 (2) Å, C(45)–C(46) = 1.50 (2) Å, and C(46)–C(45)–O = 117 (1)°) in good agreement with the expected values.

Stirring 1 in THF with an excess of NaBH$_4$ at reflux temperature for 6 h results in the formation of a yellow solution from which yellow crystals of the Rh(I) σ-acetyl [(NP$_3$)Rh(COMe)] (2) are precipitated by addition of ethanol and slow evaporation of the solvents. Compound 2 is stable in the solid state and in deareated solutions, where it behaves as a nonelectrolyte. The ^{31}P{^{1}H} NMR spectrum in CD$_2$Cl$_2$ is temperature-invariant over the temperature range +30 to −100 °C, where it exhibits an A$_3$X spin system with δ(P) 23.61 and J(PRh) = 190.9 Hz. This pattern is typical for trigonal-bipyramidal (TBP) Rh(I) complexes of NP$_3$.[3,8] The presence of a σ-bonded acetyl ligand is shown by the ^{1}H NMR spectrum in CD$_2$Cl$_2$, which contains a quartet at δ 2.03 (J(HP) = 2.7 Hz) readily

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[8] (a) Bianchini, C.; Masi, D; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Zanobini, F. *Organometallics* **1989**, *8*, 2179. (b) Bianchini, C.; Masi, D.; Mealli, C.; Meli, A.; Sabat, M. *Organometallics* **1985**, *4*, 1014.

[9] Ott, J.; Venanzi, L. M.; Ghilardi, C.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1985**, *291*, 89.

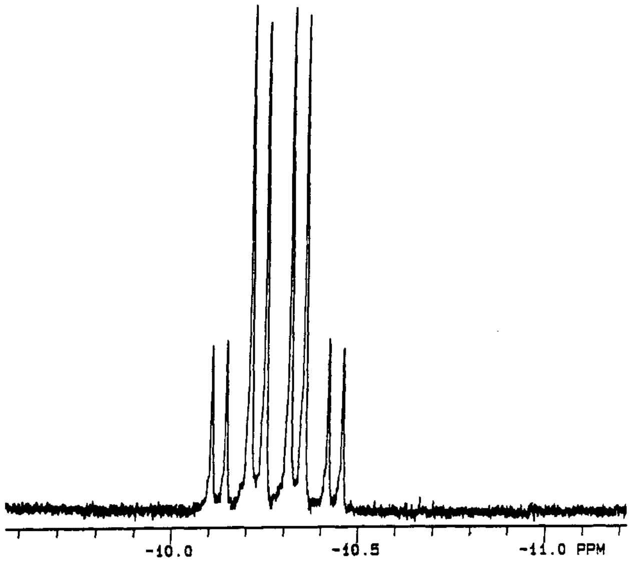

Figure 2. ^{1}H NMR resonance of the hydride ligand in [(NP_3)-Rh(H)(CO)] (CD_2Cl_2, 20 °C, 299.94 MHz, TMS reference).

attributable to the acetyl CH_3 group, and by the IR spectrum, which exhibits ν(C=O) at 1575 cm^{-1}. Interestingly, **2** can be prepared in a one-pot reaction by treatment of the monohydride [(NP_3)RhH][3] (**3**) in THF with a stoichiometric amount of methyl triflate, followed by addition of an excess of acetaldehyde and then of $NaBH_4$ in ethanol.

The **1** → **2** conversion is chemically reversible, as we have found that the hydride acetyl complex can be regenerated by reaction of **2** in THF with strong protic acids such as triflic acid. The reaction may proceed either by straightforward attack at the metal, as occurs for the conversion of the Rh(I) chloride [(NP_3)RhCl] to the Rh(III) hydride chloride [(NP_3)Rh(H)(Cl)]$^+$, or by a two-step path (i.e. protonation at the acyl oxygen, followed by hydrogen shift to the metal), as has been proposed to occur for the conversion of the Rh(I) σ-cyanide to the Rh(III) hydride cyanide [(NP_3)Rh(H)(CN)]$^+$.[10] Actually, it is worth noticing that ν(C=O) in **2** is significantly shifted to lower energy (55 cm^{-1}) as compared to that in the parent Rh(III) complex **1**. This shift suggests that the metal carbene structure Rh$^+$=CO$^-$(R) may contribute in a description of the electronic structure of the Rh–acyl moiety in **2**.[11]

Notwithstanding that the reaction between the hydride formyl complex [(NP_3)Rh(H)(CHO)]BPh_4 (**4**) with $NaBH_4$ under the conditions used for **1** does not give a stable Rh(I) σ-formyl derivative, a species of this type most likely plays an intermediate role in the formation of the hydride carbonyl [(NP_3)Rh(H)(CO)] (**5**) (ν(C≡O) 1870 cm^{-1}; ν(Rh—H) 1975 cm^{-1}).[12] In the latter compound, the central nitrogen atom of NP_3 is not coordinated to the metal, as shown by a typical infrared band at 2800 cm^{-1}.[13] The ^{31}P{^{1}H} NMR spectrum in CD_2Cl_2 consists of a temperature-invariant (from +30 to −100 °C) doublet at 13.78 ppm with J(PRh) = 125.6 Hz.[9,14] In good agreement with the ^{31}P NMR results, the ^{1}H NMR spectrum (CD_2Cl_2, 20 °C) exhibits a well-resolved doublet of quartets centered at δ 10.72 with J(HP) = 31.2 Hz and J(HRh) = 11.6 Hz (Figure 2).

The intermediacy of a formyl complex is consistent with the quantitative formation of **5** from the reaction of the σ-carbonyl [(NP_3)Rh(CO)]BPh_4 (**6**) (ν(C≡O) 1975 cm^{-1}) in THF with $NaBH_4$.[15]

Supplementary Material Available: Anisotropic thermal parameters for non-hydrogen atoms (Table IV) and bond distances and angles in the NP_3 ligand (Table V) and in the BPh_4^- counteranion of **1** (Table VI) (4 pages); a listing of observed and calculated structure factors for **1** (19 pages). Ordering information is given on any current masthead page.

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[10] Bianchini, C.; Laschi, F.; Ottaviani, M. F.; Peruzzini, M.; Zanello, P.; Zanobini, F. *Organometallics* **1989**, *8*, 893.

[11] Aktogu, N.; Felkin, H.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1982**, 1303.

[12] Bianchini, C.; Meli, A. *Organometallics* **1985**, *4*, 1537.

[13] Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics* **1983**, *2*, 1834.

[14] Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Ramirez, J. A. *Organometallics* **1990**, *9*, 226.

[15] (a) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (b) Gibson, D. H.; Owens, K.; Ong, T.-S. *J. Am. Chem. Soc.* **1984**, *106*, 1125.