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Dehydrohalogenation as a Source of $OsH_nCl(PPh_3)_3$ ($n = 1, 3$)

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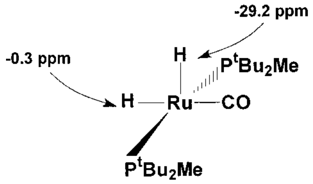
Introduction

The compound $RuHCl(PPh_3)_3$ is one of increasing and versatile utility in metal-mediated organic synthesis; initial screening for some metal-promoted organic transformation often includes $RuHCl(PPh_3)_3$.[1−6] It has the necessary (i.e., reactive) hydride ligand, it is unsaturated, and it has the bulky PPh_3 ligand, in the event that a leaving group is required during catalysis. It would therefore be desirable to have access to the osmium analogue, $OsHCl(PPh_3)_3$, to obtain different selectivity or to detect intermediates which are too transient for the ruthenium analogue. This compound was reported[7] in 1974, together with its catalytic activity for olefin hydrogenation at 50 °C. However, this work dates from before the extensive study of polyhydride complexes[8] and the knowledge of H_2 as a ligand,[9] and thus its characterization is incomplete by contemporary standards. In particular, we were attracted by the fact that the hydride chemical shift for the reported $OsHCl(PPh_3)_3$, −9.3 ppm, differed unexpectedly from that[10] of $RuHCl(PPh_3)_3$, −17.7 ppm. Moreover, there is an empirical correlation that the chemical shift of a hydride trans to an empty site in a five-coordinate species has a very high field chemical shift, certainly more negative than −15 ppm and sometimes as high as −35 ppm. For comparison,[11] see the chemical shifts in **I**. We report here a study of these points, together with a reliable synthesis of authentic $OsHCl(PPh_3)_3$ and a correct identification of the material reported earlier.[7]



Experimental Section

General. All reactions and manipulations were conducted using standard Schlenk and glovebox techniques. Solvents were dried and distilled under nitrogen or argon, and stored in airtight solvent bulbs with Teflon closures. $OsHCl(PPh_3)_3$ does not react with N_2 (1 atm, 25 °C). All NMR solvents were dried, vacuum-transferred, and stored in a glovebox under an argon atmosphere. Styrene (Aldrich) and NEt_3 (Aldrich) were degassed with freeze−pump−thaw cycles. Styrene was stored in an airtight bulb at −3 °C. $(NH_4)_2[OsCl_6]$ (Aesar) was used as received with no further purification. $OsCl_2(PPh_3)_3$ was synthesized according to published procedures.[12]

Synthesis of $[OsH_nCl(PPh_3)_3]$ ($n = 1, 3$). A 0.100 g amount of $OsCl_2(PPh_3)_3$ (0.095 mmol) was dissolved in 20 mL of benzene, and NEt_3 (0.143 mmol, 20 μL) was added to the solution. The solution was frozen, and the flask was evacuated and then filled with H_2 (600 mmHg, 0.969 mmol). The reaction mixture was allowed to warm to room temperature and stirred vigorously for 1.5 h, giving a pale green solution. At this point, the only Os-containing species (as determined by NMR-scale studies in C_6D_6) is $[OsH_3Cl(PPh_3)_3]$, characterized by a broad signal in ^1H NMR at −9.4 ppm and a ^{31}P NMR signal at 3.4 ppm in C_6D_6. The reported $^{31}P\{^1H\}$ NMR signal was located at +8.0 ppm referenced to free PPh_3 in C_6H_6, which is at 3.4 ppm when referenced to external H_3PO_4. Conversion to $[OsHCl(PPh_3)_3]$ can be accomplished by three methods.

Method A. After 1.5 h of stirring under H_2, the light green/brown suspension is evacuated to dryness, followed by addition of fresh solvent and evacuation, a total of four successive cycles, leading to a brown product which is $[OsHCl(PPh_3)_3]$.

Method B. After 1.5 h of stirring, the H_2 is removed in a vacuum (briefly) and the suspension is treated with styrene (0.096 mmol, 11 μL). This dehydrogenation can be performed at room temperature in 24 h or at 60 °C in 1 h. The dark brown solution is evacuated to dryness to give a brown solid.

Method C. The resulting $OsH_3Cl(PPh_3)_3$ solution formed in C_6D_6 was frozen, the excess H_2 was evacuated, and excess C_2H_4 was added. Within 10 min, $OsHCl(C_2H_4)_2(PPh_3)_2$ formed. The ^1H NMR spectrum showed a triplet at −1.9 ppm ($^2J_{H-P} = 22$ Hz) and $^{31}P\{^1H\}$ NMR gives a sharp peak at 0.63 ppm. When this brown solution is evacuated to dryness, the coordinated C_2H_4 is released and PPh_3 existing in solution binds again, leading to $OsHCl(PPh_3)_3$. The following NMR data are diagnostic; aromatic ^1H NMR resonances were also seen (as follows).

$OsHCl(C_2H_4)_2(PPh_3)_2$: ^1H NMR (20 °C, C_7D_8) δ −1.9 ppm (Os−H, t, $J_{HP} = 22$ Hz), δ 3.4 ppm (C_2H_4). $^{31}P\{^1H\}$ NMR (20 °C, C_7D_8) δ 0.63 ppm.

$OsH_3Cl(PPh_3)_3$: ^1H NMR (−80 °C, toluene-d_8): −11.7 ppm (br) and −4.4 ppm (br) in a 2:1 ratio. $^{31}P\{^1H\}$ NMR (−80 °C, toluene-d_8): δ −0.243 ppm (br), 7.59 ppm (d, $^2J_{P-P} = 14.6$ Hz) in a 1:2 intensity ratio.

$OsHCl(PPh_3)_3$: ^1H NMR (−70 °C, toluene-d_8) δ −24.26 ppm (dt, $^2J_{H-P} = 30$ Hz, $^2J_{H-P'} = 18$ Hz). $^{31}P\{^1H\}$ NMR (−50 °C, toluene-d_8) δ 26.03 ppm (d, $^2J_{P-P} = 11$ Hz), δ 23.85 ppm (br) in a 2:1 intensity ratio.

Results

Synthesis and Reactivity. Repetition of the literature synthesis (eq 1) produced the previously reported material in 1 h

$$OsCl_2(PPh_3)_3 + H_2 + NEt_3 \xrightarrow{C_6H_6} \qquad (1)$$

at 25 °C. We have investigated the influence of the NEt_3:Os ratio and found that a larger amount of NEt_3 replaces a second chloride, leading to the formation of $OsH_4(PPh_3)_3$.[13] The optimum ratio to avoid formation of the tetrahydride species

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(1) Mizushima, E.; Yamaguchi, M.; Yamagishi, T. *Chem. Lett.* **1997**, *3*, 237.

(2) Alibrandi, G.; Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1994**, *7*, 951.

(3) Grushin, W.; Alper, H. *J. Organomet. Chem.* **1991**, *56*, 5159.

(4) Kando, T.; Kotachi, S.; Tsuji, Y.; Watanabe, Y.; Mitsudo, T. *Organometallics* **1997**, *16*, 2562.

(5) Tsuji, Y.; Kotashi, S.; Huh, K. T.; Watanabe, Y. *J. Organomet. Chem.* **1990**, *55*, 580.

(6) Hiraki, K.; Ochi, N.; Sasada, Y.; Hayashida, H.; Fuchita, Y.; Yamanaka, S. *J. Chem. Soc., Dalton Trans.* **1985**, 873.

(7) Oudeman, A.; Van Rantwijk, F.; Van Bekkum, H. *J. Coord. Chem.* **1974**, *4*, 1.

(8) Morris, R. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, *121*, 155.

(9) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

(10) Hallman, R. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. (A)* **1968**, 3143.

(11) Heyn, R. H.; Macgregor, S. A.; Nadasdi, T. T.; Ogasawara, M.; Eisenstein, O.; Caulton, K. D. *Inorg. Chim. Acta* **1997**, *259*, 5.

(12) Hoffmann, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1974**, *97*, 4221.

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without slowing the synthesis of the desired $OsH_nCl(PPh_3)_3$ at room temperature in benzene was 1.5 equiv of NEt_3 for a period of 1.5 h.

The hydride ^1H NMR signal of the product is broad, lacking the reported resolved multiplet structure (i.e., $J_{PH} = 3$ Hz),[7] and the $^{31}P\{^1H\}$ spectrum shows only one broad signal at 3.4 ppm, all at 20 °C in benzene.

When a benzene solution of this compound is subject to vacuum removal of solvent, the NMR spectra of the resulting material in C_6D_6 at 20 °C shows an additional hydride and $^{31}P\{^1H\}$ signal. Noteworthy is the fact that the new hydride signal is significantly upfield (−23.9 ppm) of that of the original product (−9.4 ppm). We postulated that this was evidence for the operation of the equilibrium in eq 2, which vacuum-shifts

$$OsH_3Cl(PPh_3)_3 \rightleftharpoons OsHCl(PPh_3)_3 + H_2 \qquad (2)$$

to the right, by H_2 removal. The previously reported product was thus $OsH_3Cl(PPh_3)_3$, as a consequence of the synthesis being carried out under excess H_2. Indeed, if a benzene solution containing both species is saturated with H_2, NMR spectra recorded within 10 min of H_2 addition show complete disappearance of the signals attributed to $OsHCl(PPh_3)_3$. The change is immediate as judged by the solution color change from brown to pale green, together with dissolution of the less soluble $OsHCl(PPh_3)_3$, to form the more soluble $OsH_3Cl(PPh_3)_3$. Subjecting the primary synthetic product, $OsH_3Cl(PPh_3)_3$, to four benzene solvent removal cycles (i.e., strip solution to dryness, dissolve resultant solid in fresh benzene, strip, etc.) effects essentially complete disappearance of $OsH_3Cl(PPh_3)_3$. Attempts to remove H_2 by hydrogenating styrene at 25 °C show complete conversion to $OsHCl(PPh_3)_3$ and PhEt within 24 h. This conversion is conveniently carried out with equimolar styrene at 60 °C in 1 h.

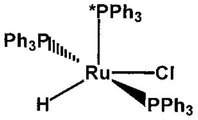
When $OsH_3Cl(PPh_3)_3$ is treated with excess ethylene at 25 °C in toluene-d_8 or CD_2Cl_2, the reagent osmium complex disappears within 10 min. This reaction is thus much faster than that with equimolar styrene. However, the product (ethane is also detected) is not merely $OsHCl(PPh_3)_3$, but rather it is that shown in eq 3. This addition and phosphine displacement is

$$OsHCl(PPh_3)_3 + nC_2H_4 \rightleftharpoons OsHCl(C_2H_4)_n(PPh_3)_2 + PPh_3 \qquad (3)$$

most evident by the hydride *triplet* in the product, and the production of free PPh_3, as seen in the $^{31}P\{^1H\}$ NMR spectrum. This reaction is reversible, and vacuum removal of volatiles also removes coordinated ethylene, to produce $OsHCl(PPh_3)_3$. The ^1H NMR spectrum at 25 °C in toluene shows separate resonances for free (5.2 ppm) and coordinated (3.4 ppm) ethylene, although the coordinated ethylene is broad. The 25 °C $^{31}P\{^1H\}$ NMR spectrum in toluene shows separate sharp lines for $OsHCl(C_2H_4)_n(PPh_3)_2$ and for added $OsHCl(PPh_3)_3$, separated by about 23 ppm. The hydride resonance is a triplet, but integration of this signal against that of coordinated ethylene, to determine n, the number of coordinated ethylenes, is not reliable since there is evidence of deuteration of free and coordinated ethylene by solvent (toluene-d_8). However, the hydride chemical shift is so far downfield (−1.9 ppm) that it indicates the presence of a ligand trans to hydride; the formula *cis,trans*-$OsHCl(C_2H_4)_2(PPh_3)_2$ is consistent with all observations.

Characterization of $OsH_nCl(PPh_3)_3$ ($n = 1, 3$). The room-temperature NMR spectra reported above are too simple for any reasonable structures for these molecules. For example, the structure[14] of $RuCl_2(PPh_3)_3$ shows a mirror-symmetric, square-pyramidal coordination sphere with two equivalent P, but one unique P. We therefore investigated the variable-temperature NMR spectra of these two osmium hydrides.

$OsHCl(PPh_3)_3$. The crystal structure of the ruthenium analogue of this compound is a useful reference point to understand the expected spectra for $OsHCl(PPh_3)_3$. The structure of $RuHCl(PPh_3)_3$ is that of a square-based pyramid (analogous to that of $RuCl_2(PPh_3)_3$), distorted by phosphine bending toward the small hydride ligand (**II**). Important distortions away from 3-fold symmetry of a trigonal bipyramid with H and Cl axial are shown by (1) the angle ∠P−Ru−P (153°), much larger than 120° (i.e., trigonal bypramid) and (2) the "apical" phosphorus, *P, being closer to Ru by 0.14 Å.[15] Below 0 °C in toluene-d_8, the $^{31}P\{^1H\}$ NMR spectrum of $OsHCl(PPh_3)_3$ begins to decoalesce, and below −30 °C, two resonances are seen in a 2:1 intensity ratio at chemical shifts which average to the single line seen at 20 °C. At −50 °C, multiplet structure can be resolved ($J_{PP'} = 11$ Hz), which is consistent with mirror symmetry (AM_2 $^{31}P\{^1H\}$ spin system). The hydride spectrum is consistent with these observations, since it is a doublet of triplets below −30 °C (AM_2H spin system with $J_{HP} = 30$ Hz, $J_{H-P'} = 18$ Hz), but then transforms, in the −20 to +20 °C region, to a quartet ($J_{HP} = 22$ Hz). On warming to 70 °C, the hydride resonance broadens, indicative of a second, distinct dynamic process (see below).



$OsH_3Cl(PPh_3)_3$. This molecule shows a 2:1 $^{31}P\{^1H\}$ NMR pattern in the range −90 to −40 °C in toluene-d_8. At −55 °C and below, multiplet structure can be resolved ($J_{PP} = 14.6$ Hz). In the range −40 to 0 °C, these coalesce to a single signal, which sharpens more at 20 °C and still further by +70 °C. The hydride signal in the range −30 to +70 °C is only one line, somewhat sharper at the higher temperatures, but never sharp enough to show resolved coupling to phosphorus. Between −55 and −50 °C, the hydride signal is too broad to detect, but decoalescence occurs below −55 °C, showing two signals in a 2:1 ratio at −11.7 and −4.4 ppm with no resolved structure.

Is this molecule a classical trihydride, or a dihydrogen complex (i.e., $OsH(H_2)$)? Measurement of T_1 of the coalesced signal in C_7D_8 at 300 MHz shows a value of 26 ms at −40 °C, which is short enough to indicate that the complex exists as $OsHCl(H_2)(PPh_3)_3$, an octahedral d^6 Os(II) complex. Poor solubility prevents lower temperature measurements, and thus obtaining a minimum T_1 value for this molecule, or for the even less soluble $OsHCl(PPh_3)_3$. The line width of the decoalesced H on Os is too broad (135 Hz at −80 °C in CD_2Cl_2) to resolve any $^1J(H-D)$ in the ^1H NMR spectrum of $OsHD_2Cl(PPh_3)_3$, made from D_2 and $OsHCl(PPh_3)_3$. It is noteworthy that the chemical shift of coordinated H_2 is *upfield* of that of the hydride ligand.

The above spectra were recorded on a solution containing both complexes, and thus in equilibrium, together with some (undetectable) quantity of H_2. The mole fraction of OsHCl-

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(13) Levison, J. J.; Robinson, D.; Uttley, H. F. *J. Chem. Soc., Dalton Trans.* **1971**, *93*, 3068.

(14) LaPlaca, S. J.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 778.

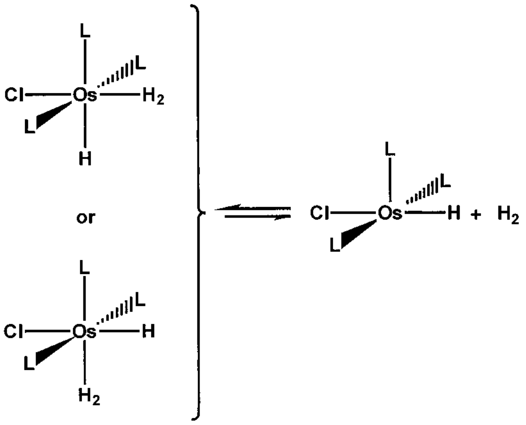
(15) Skapski, A. C.; Troughton, P. G. H. *Chem. Commun.* **1968**, 1230.

$(PPh_3)_3$ increases with increasing temperature, consistent with a positive $\Delta S°$ for eq 2. Since, even at +70 °C, separate ^1H and ^{31}P NMR signals are seen for the two species, their rate of equilibration is slower than $\sim 1\ s^{-1}$. However, the second dynamic process detected by ^1H NMR for $OsHCl(PPh_3)_3$ at +70 °C could be attributed to (1) the rate of its collision with H_2 to form $OsH_3Cl(PPh_3)_3$ or (2) dissociation of PPh_3, to form the 14-electron transient $OsHCl(PPh_3)_2$. To investigate this further, we have studied the line width of the $^{31}P\{^1H\}$ NMR signal of free PPh_3 added to $OsHCl(PPh_3)_3$. At +70 °C, we find no detectable broadening of free PPh_3, which then favors the first suggestion, above, for the origin of the broadening of the hydride signal.

It must be reiterated, however, that any ^1H or ^{31}P site exchange between $OsHCl(PPh_3)_3$ and $OsH_3Cl(PPh_3)_3$ is too slow to *coalesce* their NMR signals. Moreover, the line width of the hydride signal of $OsHCl(PPh_3)_3$ is increased by any traces of added H_2, which can also be provided, via eq 2, by any $OsH_3Cl(PPh_3)_3$ present; thus, the hydride signal of $OsHCl(PPh_3)_3$ can sometimes be broadened to the point of being very difficult to detect at +20 °C.

Conclusions

All of the observations reported here are consistent with eq 4, which emphasizes that we cannot establish with certainty whether H_2 is trans to Cl or to L (PPh_3). These two closely related species are now better characterized for organic synthetic applications, which may be further influenced by the tendency of any tris-tri*phenyl*phosphine complex to lose one PPh_3 (cf. eq 3).



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