86. ^{31}P-NMR. Measurements on Palladium-Phosphine Complexes. Nuclear *Overhauser* Effects and Spin-Lattice Relaxation Times

by **Werner Bosch** and **Paul S. Pregosin**

Laboratorium für Anorganische Chemie, ETH-Zentrum, Universitätstrasse 6, CH-8092 Zürich, Switzerland

(8.II.79)

Summary

The ^{31}P{^{1}H} nuclear *Overhauser* effects (NOE's) and ^{31}P-spin-lattice relaxation times (T_1) for a series of *trans*-[$PdCl_2P_2$], P = PEt_3, PPr_3^n, PBu_3^n, PMe_2Ph, $PMePh_2$, P(*p*-Tol)$_3$, P(cyclohexyl)$_3$ complexes are reported. Both the NOE and T_1 values depend upon the choice of solvent. The dipole-dipole mechanism dominates the spin-lattice relaxation of the coordinated phosphorus atom with the T_1 values for the PEt_3, PPr_3^n, PBu_3^n and P(cyclohexyl)$_3$ complexes decreasing with increasing molecular weight of the phosphine.

---

1. Introduction. - The utility of soluble metal-phosphine complexes as homogeneous catalysts for a variety of reactions has resulted in a increased interest in their chemistry. An important tool in the phosphine chemist's armament is ^{31}P{^{1}H}-NMR. spectroscopy. This stems directly from the relative simplicity of the ^{31}P-NMR. spectrum under conditions of broad-band proton-decoupling and the relatively large chemical range which encompasses several hundred ppm. Although many laboratories routinely employ decoupling and pulsed ^{1}H-NMR. methods in the measurement of this nuclei there are no reports concerned with either the nuclear *Overhauser* enhancement of the ^{31}P-signals (which might develop when the protons are irradiated), or the ^{31}P-spin-lattice relaxation time, T_1, in metal complexes. Since a more exact knowledge of both of these NMR. parameters can lead to a more efficient use of spectrometer time and an improvement in the spectral signal-to-noise, we have begun an investigation of these two effects in palladium complexes and report here our results for some *bis*(phosphine palladium(II)dichloride) complexes.

2. Experimental Part. - The Pd-complexes were synthesized *via* the reaction of one mol-equiv. of $PdCl_2$ with 2 mol of the appropriate tert. phosphine at room temperature (RT.) using acetone or chloroform as solvent. The complexes have all been reported previously [1] The complexes gave satisfactory ^{1}H-, ^{13}C- and ^{31}P-NMR. spectra and good microanalyses.

NMR. spectra were measured using a *Bruker* HX-90 spectrometer. ^{13}C- and ^{31}P-spectra were measured under conditions of complete proton decoupling. The T_1 measurements were performed both on samples contained in restricted volume cells designed to fit the routine 10 mm sample tube (the height of the cell is 10 mm and corresponds approximately to the height of the receiver coil) and on normal volumes (~4 ml). We observed no significant difference between the two modes. The samples were degassed (freeze-thaw cycle) and measured under N_2. The inversion-recovery method, $(180\text{-}\tau\text{-}90\text{-}T)_n$, was used to measure T_1. Typically 10-15 τ values were employed with a waiting time, T, of $>5\ T_1$. We estimate our T_1 values to be accurate to ±5%.

NOE's are thought to be ±5% and were determined from the decoupled and fully coupled spectra with at least four measurements for each complex. A decoupling power of 7-10 watts was routinely employed with the temperature held constant to avoid NOE changes due to sample heating from the RF decoupling coil.

We find $^{31}P\text{-}T_1$-values for $P(OCH_3)_3$ and $P(OEt)_3$ of 6.1 and 13.5 s, resp., which, allowing for slight differences in experimental conditions, are in reasonable agreement with the reported values of 6.5 and 12.3 s, resp. [2].

3. Results and discussion. - 3.1. *The $^{31}P\{^1H\}$ nuclear Overhauser effect.* The nuclear *Overhauser* enhancement which develops for either a ^{13}C- or ^{15}N-nucleus (*cf.* [3] resp. [4]) when the protons within the molecule are irradiated has been discussed by several groups [5]. For the case where the ^{31}P-spin-lattice relaxation is dominated by the dipole-dipole mechanism[1]), which arises from the interaction of the P-atom with the protons in the molecule, the ^{31}P nuclear *Overhauser* effect can be treated mathematically in the same way as for ^{13}C and ^{15}N and this is shown in eq. 1.

$$\mathrm{NOE} = 1 + [\gamma\,(^1\mathrm{H})/\gamma\,(^{31}\mathrm{P})]/2 \qquad (1)$$

Where mechanisms other than the dipole-dipole interaction are important the fractional nuclear *Overhauser* enhancement, η, can be expressed as shown in eq. 2, where η_0 is the enhancement for pure dipole-dipole relaxation, $T_{1_{obs}}$ is the observed, spin lattice relaxation time and $T_{1_{DD}}$ is that

$$\eta = \eta_0\,(T_{1_{obs}}/T_{1_{DD}}) \qquad (2)$$

component of T_1 which stems solely from the dipole-dipole relaxation.

From eq. 1 and 2 it is clear that the observation of an enhancement that approaches the theoretically expected value, $\eta_0 = [\gamma\,(^1H)/\gamma\,(^{31}P)]/2 = 1.24$, provides an insight into the relaxation mechanism.

In *Tables 1* and *2* we show η and T_1 values for the complexes *trans*-$[PdCl_2P_2]$, $P = PEt_3$, PPr_3^n, PBu_3^n, $P(\text{cyclohexyl})_3$, PMe_2Ph, $PMePh_2$ and $P(p\text{-Tol})_3$. The values for the enhancement, η, can be seen to range from 0.8 to 1.2, demonstrating a) that, beyond the intensity gain stemming from the collapse of multiplets, there is an enhancement of the signal intensity brought about by proton decoupling; b) that the T_1 relaxation stems mostly, and in some cases exclusively, from $^{31}P/^1H$ dipole-dipole relaxation (a similar observation has been made for a series of phosphonium salts [7] and c) that potential differences in NOE's must be considered when comparing integrals in $^{31}P\{^1H\}$-spectra.

The values η may be seen from the *Tables* to have both a solvent and temperature dependence and we shall take up these points in the next section.

---

[1]) We assume the extreme narrowing condition, $\tau_c\omega \ll 1$, that is, that the product of the rotational correlaction time, τ_c, and the nuclear resonance frequency, ω, must be much less than 1.

Table 1. *^{31}P-NOE and* T_1 *Data for the $PdCl_2P_2$ Complexes*

P		T_1 [s]	η	% DD[b]	T_1^{DD} [s]
In $CDCl_3$[a]					
PEt_3	*trans*	9.5[c]	1.0	79	12.1
PPr_3^n	*trans*	6.3	1.1	87	7.3
PBu_3^n	*trans*	4.3	1.1	92	4.7
PCy_3[e]	*trans*	3.6[d]	1.2	98	3.7
PMe_2Ph	*cis*	13.8[c]	0.9	74	18.7
	trans	13.7[c]	0.8	68	20.1
$PMePh_2$	*cis*	10.8[c]	0.9	72	15.0
	trans	10.7[c]	0.9	73	14.7
P(*p*-Tol)$_3$	*trans*	10.4[c]	0.9	71	14.6
In CD_2Cl_2[a]					
PEt_3	*trans*	14.7[c]	1.2[f]	94	15.7
PPr_3^n	*trans*	9.5	1.2[f]	96	9.9
PBu_3^n	*trans*	6.0	1.2[f]	97	6.2
PCy_3	*trans*	4.6[d][e]	1.2[f]	100	4.6
PMe_2Ph	*cis*	14.6[c]	1.0	84	17.3
	trans	18.5[c]	0.9	75	24.6
$PMePh_2$	*cis*	11.4[c]	1.1	89	12.8
	trans	15.0[c]	1.1	87	17.2
P(*p*-Tol)$_3$	*trans*	14.0[c]	1.1	91	15.4

[a] Concentration 0.1 M, Temperature 303 K, ± 1.

[b] % DD = η/η_0.

[c] Degassed.

[d] Concentration 0.01 M.

[e] Cy = cyclohexyl.

[f] The measured values for PEt_3, PPr_3^n, PBu_3^n and PCy_3 are 1.16, 1.18, 1.20 and 1.24, respectively. These have all been rounded off to 1.2.

Table 2. *^{31}P-T_1-Values: Temperature Dependence*[a] *for* trans-*[$PdCl_2(PPr_3^n)_2$]*

Temp.[b] [K]	T_1 [s]	η	% DD	T_1^{DD} [s]
323	8.2	1.1	91	9.0
303	6.3	1.1	87	7.3
283	5.5	1.1	89	6.2
263	3.2	1.1	90	3.6
243	2.1	1.1	90	2.3

[a] 0.1 M in $CDCl_3$.

[b] ±2 K.

3.2. *The ^{31}P-Spin-Lattice Relaxation Time,* T_1. After a single 90° pulse the ^{31}P magnetization decays to its equilibrium position with a characteristic time constant, T_1, the spin-lattice relaxation time [8]. This relaxation process stems from the interaction of the ^{31}P magnetic moments with random magnetic fields generated in the solution (the lattice) by the motions of the nuclei and electrons. Relatively rapid pulsing and thus rapid data accummulation will only be effective when the T_1 process is relatively efficient. $T_{1_{\text{obs}}}$ is generally expressed as shown in eq. 3, where $T_{1_{\text{DD}}}$ is the dipole-dipole contribution,

$$1/T_{1_{\text{obs}}} = 1/T_{1_{\text{DD}}} + 1/T_{1_{\text{SR}}} + 1/T_{1_{\text{CSA}}} + 1/T_{1_{\text{SC}}} \qquad (3)$$

referred to above, $T_{1_{\text{SR}}}$ is the spin-rotation contribution and stems from the interaction of the ^{31}P magnetic moment with the field generated by the movement of the molecular electron cloud, $T_{1_{\text{CSA}}}$ is the chemical shift anisotropy contribution developing from local magnetic fields due to the motion of an anisotropic section of the molecule, and T_{SC} results from changes in the local field produced at the ^{31}P nucleus due to fluctuations (nuclear relaxation or chemical changes) at a second nucleus with which the phosphorus is coupled. The term $1/T_{1_{\text{DD}}}$ can be expressed as in eq. 4 [8] (assuming the extreme narrowing condition). The terms γ represent the nuclear gyromagnetic ratios and the sum represents

$$1/T_{1_{\text{DD}}} \propto \gamma^2_{^1\text{H}} \gamma^2_{^{31}\text{P}} \sum_i \tau_c / r_i^6 \qquad (4)$$

the reorientation rate for the various ^{31}P/^{1}H dipolar interactions (in terms of a correlation time τ_c) each separated by some phosphorus-proton distance, r_i. Since we have already shown, in the previous section, that $T_{1_{\text{DD}}}$ is the dominating mechanisms, the remaining terms will not be considered further[2]).

In *Tables 1* and *2* are shown the T_1 values for our Pd-complexes and these may be seen to range from 2.1 to 18.5 seconds.

The following trends are found: a) There is a significant difference in the T_1 values for CD_2Cl_2 and $CDCl_3$ solutions with the former having larger values for all the phosphines investigated; b) the T_1 values for all of the tertiary phosphine decrease with decreasing temperature and c) for the complexes *trans*-[$PdCl_2P_2$], P = $PEt_3PPr_3^n$, PBu_3^n, P(cyclohexyl)$_3$, T_1 decreases with increasing molecular weight of the trialkyl phosphine. All three points are consistent with dipole-dipole relaxation[3]).

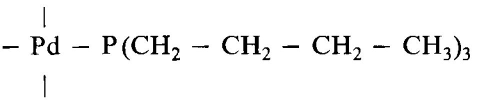
Eq. 4 predicts an inverse relationship between τ_c and T_1. Thus factors such as medium viscosity (0.406 cp and 0.519 cp for methylene chloride and chloroform, respectively, at 30° [10]) and temperature (which also affects viscosity) would be expected to markedly affect $T_{1_{\text{DD}}}$, *via* changes in τ_c. Therefore, a decrease in the sample temperature or an increase in the solution viscosity should slow molecular motions and increase the reorientation correlation time. This should decrease T_1, and this is what is observed. The solvent dependence is of practical significance since the selection of methylene chloride as solvent, instead of chloroform which sometimes contains reactive impurities, is a disadvantage from the pulsed ^{31}P-NMR. standpoint. Benzene on the other hand, with a viscosity 0.567 cp at 30°, shows T_1 values close to those of $CDCl_3$ and is often more inert (4.9 and 11.5 s for the PBu_3^n and P(p-Tol)$_3$ complexes respectively).

---

[2]) Other contributions and in particular, spin rotation, are thought to be important in determining T_1 in the free phosphines [7] [9].

[3]) Indeed the temperature dependence is a common test for the importance for the dipolar contribution since the spin rotation contribution has a reverse temperature dependence [8].

The effect on T_1 of changing the tertiary phosphine is best considered in terms of $T_{1_{DD}}$. The dependence of $T_{1_{DD}}$ on the molecular weight of the tertiary phosphine could stem from either an increase in τ_c due to the slower molecular tumbling of a higher molecular weight complex and/or an increase in the local τ_c due to slower reorientation of the phosphorus proton dipole in one segment of the molecule (in this case, the substituent on phosphorus). This type of segmental motion, and its local influence on τ_c, has been found to affect the ^{13}C relaxation in decanol [11] and a variety of other straight chain derivatives [12]. If one end of the ligand is 'anchored' (strong hydrogen bonding as in decanol, or as in our case, coordination to a metal) then that end of the chain closest to the molecular anchor reorients slower than sites further along the chain. Thus the T_1 values (in s) for the ^{13}C-atoms along the chain in $(NH_3Bu^n)(CF_3CO_2^-)$ are 3.8, 4.3, 5.0 and 5.0 for a 20% solution in D_2O [13] and decrease with increasing solution viscosity (the first carbon decreases from 3.8 to 0.44 as the viscosity (cp) increases from 0.95 to 9.1). In order to test this possibility for our system we have determined the ^{13}C-T_1-values (in s) for *trans*-$[PdCl_2(PBu_3^n)_2]$ and these are shown in the *Scheme*. The data suggest that the segmental motion concept is valid for our derivatives.



$-Pd-P(CH_2-CH_2-CH_2-CH_3)_3$

0.36 0.55 1.10 2.45 1.0 M in $CDCl_3$

Further, since the ^{13}C-T_1 of the carbon atom nearest a molecular anchor (see *Scheme* for $CH_3(CH_2)_nBr$) and the T_1 of the ^{31}P-atom in our trialkylphosphine complexes each decrease with increasing alkyl chain length we conclude that similar

$Br-CH_2(CH_2)_nCH_3$ [15]

T_1 [s]	11.6	8.0	6.6	4.7	3.6
n	2	3	4	5	6

'anchoring' effects are operating to change the ^{31}P-T_1-values in our complexes. An interesting consequence of the molecular weight dependence is that complexes containing non-equivalent phosphine ligands of different molecular weight need not show NMR. integrals which correspond to the correct number of P-atoms.

Table 1 shows that the aryl containing phosphines have longer T_1 values than the trialkyl phosphines. This may be attributed to the smaller number of protons situated on the first C-atom along the substituent and thus to less efficient dipole-dipole relaxation. Based on the known [15] X-ray structure for *cis*-$[PdCl_2(PMe_2Ph)_2]$ we calculate a P–H distance of 2.41 Å for the CH_3 group and a P–H distance of 3.9 Å for the *ortho* protons of the phenyl group. Since eq. 4 contains a $1/r^6$ term, the dipole-dipole interaction for the aromatic protons will be much less efficient.

Since the P-atoms in the complexes can be relaxed by several different types of protons, each at different distances from the P-atom, the calculation of τ_c is somewhat complicated. The various protons may be moving at different speeds in different sections of the molecule. Despite this it is useful to calculate an average τ_c for our complexes, using the measured $T_{1_{DD}}$ values and the calculated r_i values in order to have a first estimate of the magnitude τ_c. Using the values in *Table 1* and P–C–H, P–C–C–H (staggered, aliphatic chains) and P–C–C–H (aromatic) distances of 2.41, 3.54 and 3.89 Å respectively, we calculate τ_c values between 10^{-10} and 10^{-11} sec for our complexed P-atoms.

Thanks are due to *R. W. Kunz* for helpful discussions.

REFERENCES

[1] *S.O. Grim & R. Keiter,* Inorg. chim. Acta *4,* 56 (1970); *J.N. Jenkins & B.L. Shaw,* J. chem. Soc. A *1966,* 770.
[2] *S.W. Dale & M.E. Hobbs,* J. phys. Chemistry *75,* 3537 (1971).
[3] *K.F. Kuhlman & D.M. Grant,* J. Amer. chem. Soc. *90,* 7355 (1968).
[4] *R.L. Lichter & J.D. Roberts,* J. Amer. chem. Soc. *93,* 3200 (1971). *G.E. Hawkes, W.M. Litchman & E.W. Randall,* J. magn. Res. *19,* 255 (1975).
[5] *J.H. Noggle & R.E. Schirmer,* 'The Nuclear Overhauser Effect, Chemical Applications', Academic Press, New York & London 1971.
[6] *J. Solomon,* Phys. Rev. *99,* 559 (1955).
[7] *H. Beierbeck, R. Martino, J.K. Saunders & C. Benezra,* Canad. J. Chemistry *54,* 1918 (1976).
[8] For an introduction to pulsed NMR. and relaxation phenomena see *T.C. Farrar & E.D. Becker* 'Pulse and Fourier Transform NMR', Academic Press 1971.
[9] *N.J. Koole, A.J. de Koning & M.J.A. de Bie,* J. magn. Res. *25,* 375 (1977).
[10] *Landolt-Börnstein,* 'Physical Chemistry Tables', Vol. 1, Springer-Verlag 1923.
[11] *D. Doddrell & A. Allerhand,* J. Amer. chem. Soc. *93,* 1558 (1971).
[12] *G.C. Levy,* Accts. of Chem. Res. *6,* 161 (1973).
[13] *G.C. Levy, R.A. Komoroski & J.A. Halstead,* J. Amer. chem. Soc. *96,* 5456 (1974).
[14] *Y.K. Levine, N.J.M. Birdsall, A.G. Lee, J.C. Metcalfe, P. Partington & G.C.K. Roberts,* J. chem. Physics *60,* 2890 (1974).
[15] *L.L. Martin & R.A. Jacobson,* Inorg. Chemistry *10,* 1795 (1971).

---

87. Syntheses of (+)-(*S, S*)-(*cis*-6-Methyltetrahydropyran-2-yl)acetic Acid and of (−)-(*R, R*)-Didesoxy-pyrenophorine Using a New d^5-Reagent[1])[2])

Preliminary communication

by **Dieter Seebach** and **Manat Pohmakotr**

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum,
Universitätstrasse 16, CH-8092 Zürich

(1.III.79)

Summary

The Li/K-derivative **6** is used to synthesize the title compounds (**3a** and **4a**) in enantiomerically pure form from (−)-(*S*)-propylene epoxide. The C,C bond

---

[1]) The work described here was done in 1977, see PhD-Thesis of *M.P.*, Justus-Liebig-Universität, Giessen, Oct. 1978.

[2]) The acceptor (a)/donor (d) nomenclature of synthetic methodology and a classification of the methods of reactivity *umpolung* are described in a review article [3]. According to this nomenclature, an enolate, an enone, and a dienone are d^2-, a^3-, and a^5-reagents, respectively.