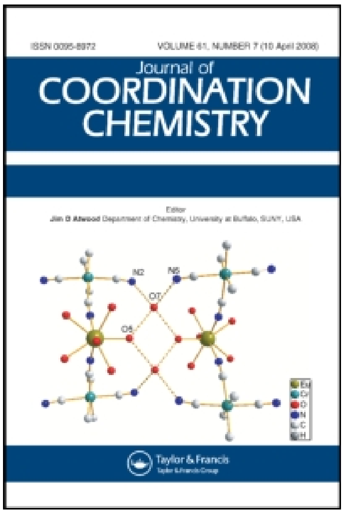

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Mynott, R. J. , Pregosin, P. S. and Venanzi, L. M.(1973) 'A PHOSPHORUS-31 NUCLEAR MAGNETIC RESONANCE STUDY OF THE TUNGSTEN COMPLEXES OF A TERDENTATE AND A QUADRIDENTATE PHOSPHINE', Journal of Coordination Chemistry, 3: 2, 145 — 148

To link to this Article: DOI: 10.1080/00958977308073801

URL: http://dx.doi.org/10.1080/00958977308073801

J. Coord. Chem.
1973, Vol. 3, pp. 145–148

A PHOSPHORUS-31 NUCLEAR MAGNETIC RESONANCE STUDY OF THE TUNGSTEN COMPLEXES OF A TERDENTATE AND A QUADRIDENTATE PHOSPHINE

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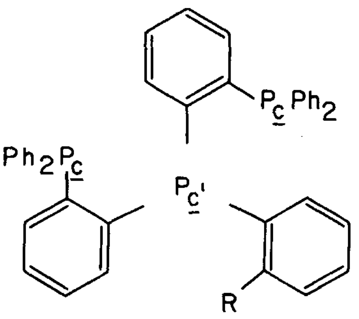
(*Received January 23, 1973; in final form April 10, 1973*)

The phosphorus-31 nmr spectra of $[W(CO)_3(TP)]$ and $[W(CO)_3(QP)]$ ($TP = (o\text{-}Ph_2P \cdot C_6H_4)_2PPh$) and $QP = (o\text{-}Ph_2P \cdot C_6H_4)_3P$ have been measured using continuous wave and Fourier transform techniques. From the $^1|J_{^{183}W-^{31}P}|$ values, it is deduced that both molecules have the facial arrangement of carbonyl groups. Relative signs of some phosphorus–phosphorus couplings in $[W(CO)_3(QP)]$ are reported and it is shown that they cannot be used for stereochemical assignment in complexes of ligands such as QP. The phosphorus-31 spectra of the free ligands TP and QP are typical of the classes AB_2 and AB_3, respectively, and their $^3|J_{P_a-P_b}|$ values (154.0 and 155.8 Hz, respectively) are among the largest constants of their type observed to date.

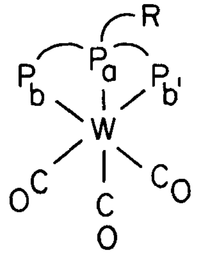
INTRODUCTION

The reaction of tungsten hexacarbonyl with tridentate ligand bis(*o*-diphenylphosphinophenyl)-phenylphosphine, TP, Ia, and with the quadridentate ligand tris(*o*-diphenylphosphinophenyl)phosphine, QP, Ib, gives products of the type $[W(CO)_3(L)]$ (L = TP or QP).[1]

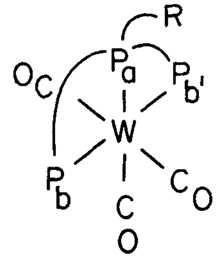


R = H, TP, **Ia**;
R = Ph_2P_c, QP, **Ib**.

Low resolution nmr studies[2] show that one of the terminal donor atoms of QP in $[W(CO)_3(QP)]$ is not bonded to the tungsten atom but do not answer the structural question as to whether the three carbonyl groups in complexes $[W(CO)_3(L)]$ (L = TP or QP) occupy *vicninal*, **II**, or *meridional*, **III**, positions.



R = Ph, **IIa**;
R = $o\text{-}C_6H_4 \cdot P_cPh_2$, **IIb**;



R = Ph, **IIIa**;
R = $o\text{-}C_6H_4 \cdot P_cPh_2$, **IIIb**.

Furthermore, the interpretation of the nmr data for $[W(CO)_3(QP)]$ is complicated by the observation that all four phosphorus atoms of the ligand QP appear to be magnetically inequivalent,[2] i.e., the terminal donor atoms bonded to the metal atom labelled P_b and $P_{b'}$ appear to be in different magnetic environments, while this is not the case for $[W(CO)_3(TP)]$. As there appears to be a correlation between the magnitude of the $^1|J_{^{183}W-^{31}P}|$ coupling constants and the geometry of the complexes containing these two atoms,[3] the compounds $[W(CO)_3(L)]$ (L = TP and QP) were re-examined under high resolution conditions. During the course of this work, we also re-examined the spectra of the free ligands TP and QP.

EXPERIMENTAL

The organic ligands TP and QP were prepared by the method of Chiswell and Venanzi,[4] and the complexes as described by Howell and Venanzi.[5] Continuous wave phosphorus-31 nmr spectra were measured on a Varian HA-100D nmr spectrometer, operating at 40.5 MHz, using 5 mm o.d. tubes. When necessary, a Varian C-1024 time-averaging computer was employed to accumulate sufficient signal to observe a spectrum. The measurements of $^1|J_{^{183}W-^{31}P}|$ were made employing a Bruker HX-90 spectrometer operating at 36.4 MHz, equipped with Fourier Transform (FT) facilities. In this case, 10 mm o.d. tubes were used. The phosphorus-31 spectrum of [W(CO)$_3$(TP)] was obtained by transforming the free induction decay which resulted from the accumulation of 6500 8 μ sec-pulses spaced 0.8 sec apart using a Nicolet 1085 computer system. In a similar manner, the spectrum of [W(CO)$_3$(QP)] was obtained after 2000 6 μ sec-pulses. For both the CW and FT measurements, simultaneous broad-band decoupling of protons was employed.

All compounds were examined in saturated dichloromethane solutions, and chemical shifts are reported relative to external 85% H_3PO_4 and are considered accurate to ±0.5 ppm.

RESULTS AND DISCUSSION

The phosphorus-31 nmr spectra of the free ligands TP and QP are typical of the classes AB_2 and AB_3, respectively[6] and were analyzed using known methods.[7] The relevant parameters are given in the Table. It is interesting to note that the resonance positions of these phosphorus atoms are at a significantly higher field than that for triphenylphosphine itself ($\delta = -5.6$ ppm). The $^3|J_{P_a-P_b}|$ values for both TP (154.0 Hz) and QP (155.8 Hz) are among the largest three-bond phosphorus–phosphorus couplings observed to date.[8]

The spectrum of [W(CO)$_3$(TP)] (see Table) is that of an AX_2 system with a $|J_{P_a-P_b}|$ value of 4.9 Hz. Such small coupling constants are typical of complexes of related ligands, e.g., [PdCl(QP)]Cl and [Ir(CO)(QP)] [BPh$_4$] have $|J_{P_a-P_b}|$ values of 5.9 and 16.3 Hz, respectively.[9]

TABLE I
Nmr Parameters of TP, QP, [W(CO)$_3$(TP)] and [W(CO)$_3$(QP)]. (The phosphorus atom labels are given in structures **I**, **II** and **III**)

	TP	QP	[W(CO)$_3$(TP)]	[W(CO)$_3$(QP)]
δ_a	–	–	+68.0[a]	+76.0
δ_b	–	–	+43.6	+43.2
$\delta_{b'}$	–	–	–	+50.2
δ_c	−13.5	−13.1	–	−14.4
$\delta_{c'}$	−16.6	−19.5	–	–
J_{W-P_a}	–	–	223[b]	228
J_{W-P_b}	–	–	224	224
$J_{W-P_{b'}}$	–	–	–	217
$J_{P_a-P_b}$	–	–	–	4.0
$J_{P_a-P_{b'}}$	–	–	4.9	9.2
$J_{P_a-P_c}$	–	–	–	59.8
$J_{P_b-P_{b'}}$	–	–	–	20.8
$J_{P_b-P_c}$	–	–	–	4.4
$J_{P_c-P_{c'}}$	154.0	155.8	–	–

[a] In ppm relative to external H_3PO_4 and estimated to be correct to ±0.5 ppm.
[b] In Hz, ±1.

The spectrum of [W(CO)$_3$(QP)] (see Figure and the Table) is more complex and assignable to the class AMQX, i.e., with four individual phosphorus resonances. On first inspection such a spectrum would seem inconsistent with structures **IIb** and **IIIb** as these might be expected to give spectra typical of AM_2X systems with P_b and $P_{b'}$ representing the M resonances. The presence of a trailing o-$PH_2P \cdot C_6H_4$-group in this complex is supported by the observation of a resonance at −14.4 ppm., which occurs in a range which is characteristic of uncoordinated phosphorus atoms in QP-type ligands.[2] The other resonances have also been assigned using previous data on related complexes,[2] i.e., the resonance at lowest field is assigned to P_a and the other two resonances to P_b and $P_{b'}$. The non-equivalence of P_b and $P_{b'}$ is likely to be caused by the presence of the trailing o-$Ph_2P \cdot C_6H_4$-group. Molecular models indicate that it is not possible to arrange this group in a symmetrical position between P_b and $P_{b'}$ so that it must lie closer to either of these two atoms upsetting the apparent magnetic equivalence. As reported earlier, also the complex [Cr(CO)$_3$(QP)] shows an AMQX phosphorus-31 spectrum.[2]. The phosphorus–phosphorus couplings in [W(CO)$_3$(QP)] may be seen to vary from ca. 4–60 Hz. The value of $^3|J_{P_a-P_c}|$ (59.8 Hz) is not unusual if one considers that complex formation may cause both a decrease in magnitude and a change in sign of $^3J_{P-P}$. Bertrand, *et al.*,[10] have shown this to occur for $P(OCH_2)_3P$ which has a $^3J_{P-P}$ of −37.2 Hz while [W(CO)$_5${P(OCH$_2$)$_3$P}] and [W$_2$(CO)$_{10}${P(OCH$_2$)$_3$P}] have $^3J_{P-P}$ values of −0.4 and +73.8 Hz, respectively. The significance of the magnitudes of the remaining J_{P-P} values is less

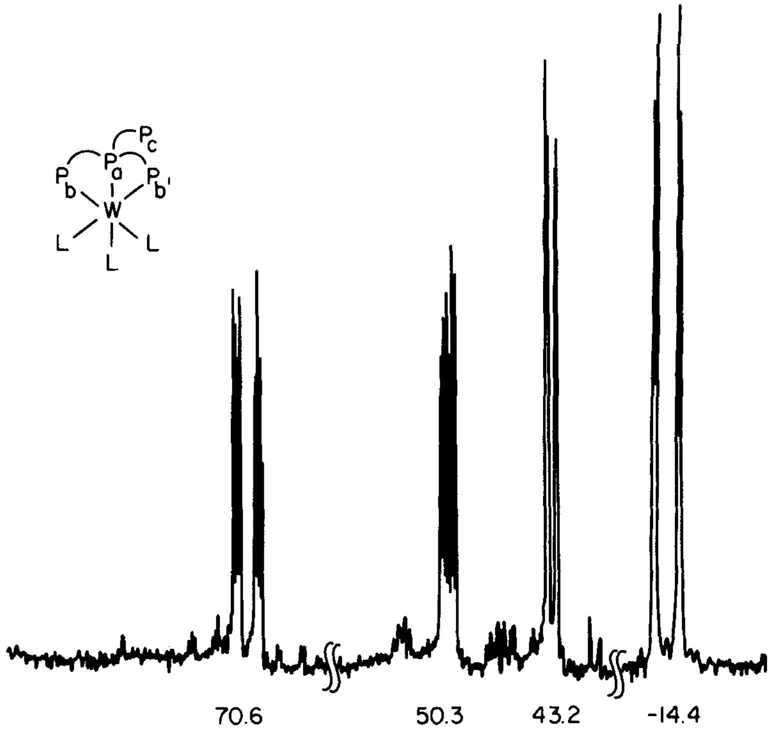


FIGURE 1 The phosphorus-31 nmr spectrum of [W(CO)$_3$(QP)]

certain. It is, however, tempting to suggest that the atom $P_{b'}$ in complex **IIb** is the atypical one on the grounds that (1) δ_{P_b} in [W(CO)$_3$(QP)] is 43.2 ppm and the analogous phosphorus position in [W(CO)$_3$(TP)] is 43.6 ppm. (2) there is good agreement between $J_{P_a-P_c}$ in the former compound (4.0 Hz) and J_{P-P} in the latter (4.9 Hz).

It is possible to establish the stereochemistry of complexes [W(CO)$_3$(L)] (L = QP and TP) by measuring the coupling constants $^1|J_{^{183}W-^{31}P}|$. Grim, *et al.*,[3] have shown that complexes *cis-* and *trans-*[W(CO)$_4$(R$_3$P)$_2$] have $^1|J_{^{183}W-^{31}P}|$ values in the ranges 220–230 and 260–270 Hz, respectively. The tungsten-183 satellites[11] for [W(CO)$_3$(TP)] and [W(CO)$_3$(QP)] were obtained using pulsed nmr techniques in conjunction with Fourier Transform facilities and it was found that all the coupling constants were in the range 217–228 Hz showing that the complexes are to be assigned structures **IIa** and **IIb**, respectively.

Ogilvie, *et al.*,[12] have shown that the stereochemistry of complexes of the type *cis-* and *trans-*[W(CO)$_4$(R$_3$P)$_2$] is also obtainable from the $^2J_{PP}$ coupling constants, i.e., the *cis*-isomers have $^2J_{PP}$ values in the range −13.4 to −38 Hz and the *trans*-isomers in the range +65 to +315 Hz. This criterion, however, is not necessarily applicable to complexes of the ligands QP and TP as, in these cases, the observed J_{PP} values may consist of components such as $^3J_{PP}$ as well as $^2J_{PP}$ which may differ widely both in magnitude *and* sign. In order to test the validity of the $^2J_{PP}$ criterion for structural assignment, in complexes of our ligands, a relative sign determination using the double resonance method[13] was undertaken. Using this method, it was found that $J_{P_aP_b}$ and $J_{P_bP_{b'}}$ have opposite signs while $J_{P_aP_b}$ and $J_{P_aP_c}$ have the same sign. Thus, the $^2J_{PP}$ criterion indicates that compounds [W(CO)$_3$(L)] (L = TP and QP) should be assigned geometry **III** showing that this criterion cannot be used in complexes of ligands such as TP and QP.

In the preparative paper[1] infrared stretching frequencies for the carbonyl groups in [W(CO)$_3$(L)] were reported. It should be noted here that while their pattern of bands in the carbonyl region is similar to that found for compounds *fac*-[M(CO)$_3$(L)$_3$],[14] it was felt that, given the complex nature of the organic ligands, a structure arrangement should be based on more reliable criteria.

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