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The First Observation of ^1J(Ru,P) in ^{31}P CP/MAS NMR Spectra of Solid Ruthenium Compounds

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Indirect spin–spin coupling constants involving phosphorus-31 and metal nuclei provide an important parameter for characterizing metal–phosphorus bonds.[2–6] For example, the magnitude of $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ in square-planar Pt(II) phosphine complexes provides unambiguous stereochemical information.[2–8] One-bond ^{31}P–M spin–spin coupling constants are now available for more than 20 different metals.[4] Most of the data involve metal nuclei which have a spin $^1/_2$ isotope (e.g., ^{103}Rh, $^{107/109}$Ag, $^{111/113}$Cd, $^{117/119}$Sn, ^{183}W, ^{187}Os, ^{195}Pt, ^{199}Hg, ^{207}Pb).[2–6] Phosphorus couplings involving quadrupolar metal nuclei ($S \geq 1$) are difficult or impossible to observe in solution NMR studies because of the efficiency of the quadrupolar relaxation mechanism in all but the most symmetric metal environments.[9–11] Hence, coupling constants such as $J(^{59}\mathrm{Co},^{31}\mathrm{P})$[11] and $J(^{99}\mathrm{Tc},^{31}\mathrm{P})$[12] are only observed in relatively symmetric octahedral complexes where the electric field gradient at the quadrupolar ^{59}Co ($S = {}^7/_2$) or ^{99}Tc nucleus ($S = {}^9/_2$) is approximately zero. In 1982 Menger and Veeman[13] demonstrated that analysis of ^{31}P CP/MAS spectra of solid Cu(I) phosphine complexes provides $J(^{63}\mathrm{Cu},^{31}\mathrm{P})$ and $J(^{65}\mathrm{Cu},^{31}\mathrm{P})$, even though both of these naturally occurring copper isotopes are quadrupolar with $S = {}^3/_2$. Subsequently, several reports of values for $J(^{63/65}\mathrm{Cu},^{31}\mathrm{P})$ have appeared in the literature.[14] More recently, Lindner et al.[15,16] and Gobetto et al.[17] reported observations of $^1J(\mathrm{M},^{31}\mathrm{P})$ from solid-state NMR studies where M = $^{95/97}$Mo, ^{55}Mn, ^{59}Co, and ^{93}Nb. Despite the interest in and catalytic importance of ruthenium complexes, only two reports of coupling constants involving the quadrupolar ruthenium-99 nucleus have appeared, viz., $J(^{99}\mathrm{Ru},^{13}\mathrm{C})$ and $J(^{99}\mathrm{Ru},^{17}\mathrm{O})$ in the highly symmetric compounds $K_4[Ru(CN)_6]$ and RuO_4, respectively,[18] and $J(^{119}\mathrm{Sn},^{99}\mathrm{Ru})$ in $[Ru(SnCl_3)_5Cl]^{4-}$.[19] Here we wish to report the first observation of $^1J(^{101,99}\mathrm{Ru},^{31}\mathrm{P})$ in ^{31}P CP/MAS NMR spectra of solid ruthenium–phosphorus complexes.

The center peak in the 81.0-MHz ^{31}P CP/MAS NMR spectrum of the octahedral complex *all-trans*-$Ru(PEt_3)_2(CO)_2(C{\equiv}CPh)_2$ (**1**)[20] is shown in Figure 1a. Particularly striking are the small satellite peaks arising from Ru,P spin–spin coupling, which surround the intense isotropic peak, $\delta(^{31}\mathrm{P})$ = 18.7 ppm (enlarged in Figure 1b). Since ruthenium-99 (natural abundance 12.7%) and ruthenium-101 (17.1%) both have a nuclear spin of $^5/_2$,[21,22] one might anticipate the high-resolution ^{31}P NMR spectrum of a molecule containing the ^{101,99}Ru,^{31}P spin-pairs to consist of six equally spaced peaks, each associated with one of the allowed components of ^{101,99}Ru nuclear spin along the magnetic field, m_s. However, it is well-known that in the solid state the Zeeman levels of a quadrupolar nucleus are strongly perturbed by the quadrupolar interaction and hence the quantum numbers, m_s, are no longer eigenstates of the Zeeman-quadrupolar Hamiltonian.[23–26] One important consequence of the so-called breakdown of the high-field approximation is that dipolar interactions

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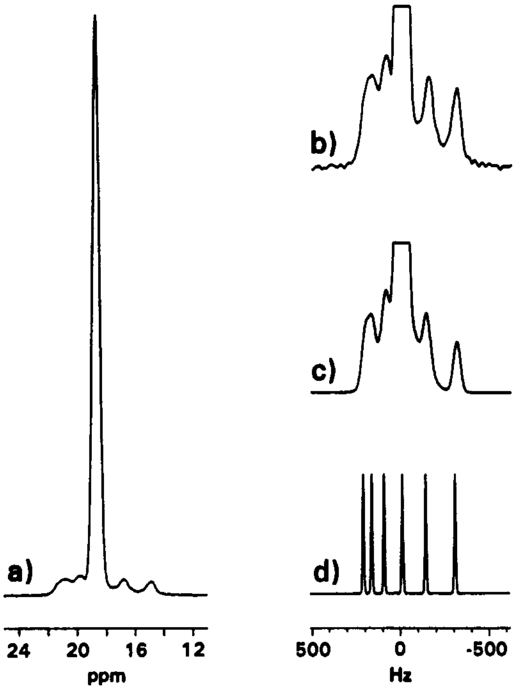

Figure 1. (a) Isotropic region of the 81.0-MHz ^{31}P CP/MAS NMR spectrum of *all-trans*-$Ru(PEt_3)_2(CO)_2(C\equiv CPh)_2$ (**1**). (b) Amplification of the satellite peaks shown in (a). (c) Calculated spectrum due to 70% of uncoupled phosphorus-31 and 13% coupled to ruthenium-99 ($J = 104$ Hz, $d = -46$ Hz). (d) Schematic representation of the ruthenium-99 satellites.

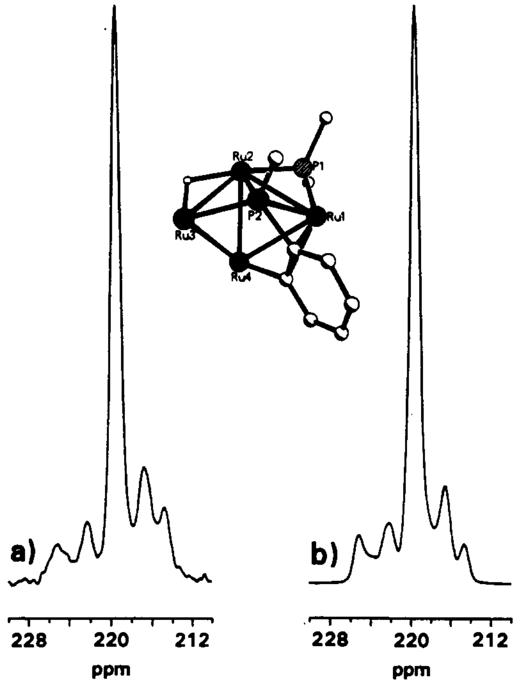

Figure 2. Isotropic region of the 81.0-MHz ^{31}P CP/MAS NMR spectrum of the butterfly cluster $(\mu\text{-}H)Ru_4(CO)_{10}(\mu\text{-}PPh_2)[\mu_4\text{-}PPh(C_6H_4)]$ (**2**) in the μ-PPh_2 region: (a) experimental spectrum; (b) calculated spectrum. The skeletal framework of **2** is shown in the insert.

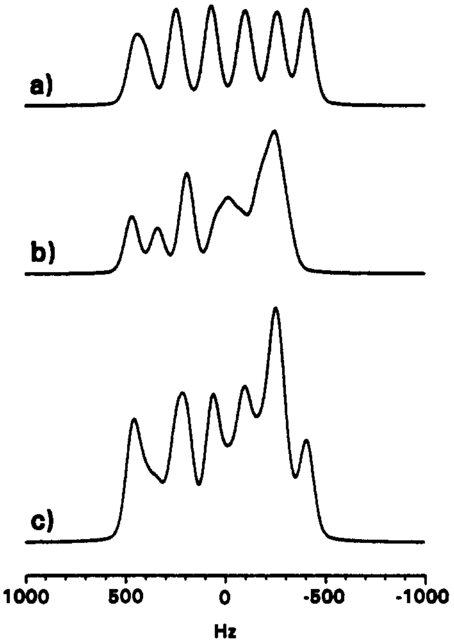

Figure 3. (a, b) Calculated ^{31}P NMR spectra of the $^{99}Ru,^{31}P$ and $^{101}Ru,^{31}P$ spin pairs at each of the two sites, respectively, of the butterfly cluster **2**. (c) Sum of the spectra shown in (a) and (b). This sum corresponds to the satellite peaks shown in Figure 2b.

involving quadrupolar nuclei are not completely eliminated by magic angle spinning.[27] As a result, high-resolution MAS NMR spectra of spin $^1/_2$ nuclei which are *J*-coupled to quadrupolar nuclei are not generally symmetrical. Instead, the separations between peaks are "squeezed" at one end and "stretched" at the other (Figure 1d).[28] Two parameters, *J* and the residual dipolar coupling *d*, are required to describe these multiplets.

Despite the apparent complexity of the spin $^1/_2$, spin *S* system, it is important to recognize[28] that *J* and *d* can be readily determined from an analysis of the high-resolution MAS NMR spectrum of the spin $^1/_2$ nucleus. Adjacent peaks in the ^{31}P CP/MAS spectrum of $^{101,99}Ru,^{31}P$ spin-pairs will be separated by $|J| - 6d/5$, $|J| - 3d/5$, $|J|$, $|J| + 3d/5$, and $|J| + 6d/5$, starting at the low frequency end and assuming $|J| > |d|$. Note that despite the asymmetry of the multiplet (Figure 1d), the separation between the outermost peaks still equals $|5J|$. For the octahedral compound **1**, the ^{31}P NMR line shape in Figure 1b was simulated (Figure 1c) with $J = 104$ Hz and $d = -46$ Hz. The parameter *d* is related to the characteristics of the electric field gradient (EFG) at the ruthenium nucleus and hence to the ruthenium quadrupolar coupling constant χ and its asymmetry.[28] If the largest component of the EFG tensor in **1** is along the P–Ru–P bond axis, $\beta = 0°$ and $\chi = 8.5$ MHz, independent of the value of η. On the other hand, if the largest component of the EFG tensor is along either the PhC≡C—Ru—C≡CPh or O≡C—Ru—C≡O axis, then $\beta = 90°$ and $\alpha = 0$ or 90°; therefore, it is impossible to obtain χ and η independently. There is no firm experimental information regarding the orientation of the EFG tensor; however, Mössbauer studies have indicated similar partial quadrupolar splittings for

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(28) To first order, the spin $^1/_2$ (^{31}P) MAS NMR transitions of a spin $^1/_2$, spin *S* pair are given by[27]

$$\nu_m(^{31}P) = -m|J| - [S(S+1) - 3m^2]d/S(2S-1)$$

where $|J|$ is the $^{101,99}Ru$ indirect spin–spin coupling constant, $S = {}^5/_2$ for $^{101,99}Ru$, $m = {}^5/_2, {}^3/_2, ..., -{}^5/_2$, and *d* is given by

$$d = -(3\chi D/20\nu_s)[(3\cos^2\beta - 1) + \eta\sin^2\beta\cos 2\alpha]$$

D is the Ru–P direct dipolar coupling constant, dependent on the inverse cube internuclear separation, ν_s is the ^{99}Ru or ^{101}Ru Larmor frequency (9.23 and 10.34 MHz at $B_0 = 4.7$ T), χ is the ^{99}Ru or ^{101}Ru nuclear quadrupolar coupling constant, $e^2q_{zz}Q/h$, and η is a parameter which describes the asymmetry of the electric field gradient (EFG) tensor at the nucleus S, $(eq_{xx} - eq_{yy})/eq_{zz}$, with $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$. The azimuthal and polar angles α and β define the orientation of the $^{101,99}Ru,^{31}P$ dipolar vector in the principal axis system of the EFG tensor. Note that, to first order, the appearance of the spectrum is independent of the sign of *J*.

PR_3 and CO ligands,[29] implying that the largest component of the EFG tensor is along the acetylide–Ru bonding axis. If one further assumes that $\eta \approx 0$, then $\chi \approx -17$ MHz. We believe that this is the correct order of magnitude for χ(Ru) in **1**, although the error in this value might be considerable. Interestingly, direct measurements of χ values for ^{99}Ru via NQR spectroscopy have not been reported.[31] Note that, in principle,[28] the NMR experiment contains information on both the magnitude and sign of χ.

The ^{31}P CP/MAS NMR spectrum of **1** (Figure 1) gives no evidence for ^{101}Ru,^{31}P spin–spin coupling. Signal intensity from the ^{101}Ru,^{31}P spin-pair appears to be absent from the spectrum. Although the magnetogyric ratios are similar [$\gamma(^{101}\mathrm{Ru})/\gamma(^{99}\mathrm{Ru}) = 1.121$], the quadrupolar moment, Q, of ^{101}Ru is 5.8 times that of ^{99}Ru. Three consequences of the large Q for ^{101}Ru are as follows: (i) The value of d for the ^{101}Ru,^{31}P spin-pair will be ~5.8 times the corresponding value for the ^{99}Ru,^{31}P spin-pair. Simulations show that while $J(^{101}\mathrm{Ru},^{31}\mathrm{P})$ and $J(^{99}\mathrm{Ru},^{31}\mathrm{P})$ are similar, the distortions of the six-line multiplets due to $d(^{101}\mathrm{Ru})$ and $d(^{99}\mathrm{Ru})$ are sufficiently different to produce additional peaks in the spectrum. Absence of these features indicates that only the ^{99}Ru,^{31}P spin-pair is present. (ii) Because of the large value of $\chi(^{99}\mathrm{Ru})$ derived for **1** (−17 MHz), we estimate $\chi(^{101}\mathrm{Ru}) \gg \nu(^{101}\mathrm{Ru})$. The first-order perturbation approach used here for ^{99}Ru,^{31}P couplings will not be valid for ^{101}Ru,^{31}P couplings.[27] (iii) Since the relaxation rate of quadrupolar nuclei depends on χ^2, ^{101}Ru relaxation will be approximately 33.5 times more efficient than that of ^{99}Ru. This could result in self-decoupling of ^{101}Ru from ^{31}P.

We have observed ^{99,101}Ru satellites in the ^{31}P CP/MAS spectrum of the ruthenium–phosphido butterfly cluster $(\mu\text{-H})\text{-}Ru_4(CO)_{10}(\mu\text{-}PPh_2)[\mu_4\text{-}PPh(C_6H_4)]$ (**2**).[32] An expansion of the ^{31}P CP/MAS peaks due to the μ-PPh_2 group is shown (Figure 2) together with the calculated spectrum. To obtain a satisfactory simulation, two different nonequivalent ruthenium sites were introduced (Figure 3), in agreement with the known structure,[32] and both isotopes, ^{101}Ru and ^{99}Ru, taken into account. Ratios of $J(^{101}\mathrm{Ru},^{31}\mathrm{P})/J(^{99}\mathrm{Ru},^{31}\mathrm{P})$ and $d(^{101}\mathrm{Ru})/d(^{99}\mathrm{Ru})$ were fixed for each site to 1.121 and 5.8, respectively. The spectrum shown (Figure 2b) was calculated using $J(^{101}\mathrm{Ru},^{31}\mathrm{P}) = 174$, $d(^{101}\mathrm{Ru}) = +24$, $J(^{99}\mathrm{Ru},^{31}\mathrm{P}) = 159$, and $d(^{99}\mathrm{Ru}) = +4$ Hz for site 1 and $J(^{101}\mathrm{Ru},^{31}\mathrm{P}) = 145$, $d(^{101}\mathrm{Ru}) = +108$, $J(^{99}\mathrm{Ru},^{31}\mathrm{P}) = 129$, and $d(^{99}\mathrm{Ru}) = +19$ Hz for site 2. A comparison of these d values reveals that (i) the two ruthenium sites Ru(2) and Ru(1) in cluster **2** differ widely, indicating distinct structural and bonding differences for the wingtip and hinge ruthenium atoms in the Ru_4 butterfly, and (ii) the values of d for **2** have opposite signs compared to that for the octahedral complex **1**. Since the orientation of the EFG tensor for **2** is unknown, the change in sign may be due to a change in the sign of χ or the sign of the orientational term.[28] However, since both spin-pairs, ^{101}Ru,^{31}P and ^{99}Ru,^{31}P, were observed in the ^{31}P CP/MAS NMR spectrum of the cluster **2**, χ is assumed to be significantly smaller than for the octahedral complex **1**. This is at first sight surprising, but Mössbauer studies have shown that the iron cluster $Fe_3(CO)_{12}$ exhibits significantly smaller quadrupolar splittings than octahedral iron complexes of low symmetry.[30a]

Table I. Magnetogyric Ratios and Typical Values of Indirect and Reduced Spin–Spin Coupling Constants, J and K, Respectively

nucleus	γ, 10^7 rad s^{-1} T^{-1}	$J(\mathrm{M},^{31}\mathrm{P})$, Hz	$K(\mathrm{M},^{31}\mathrm{P})$, 10^{19} N A^{-2} m^{-3}
^{57}Fe	0.8687	26–147[a,b]	164–930
^{99}Ru	−1.2286	100–174	447–796
^{187}Os	0.6193	71–317[b,c]	630–2813
^{59}Co	6.3015	414–1222[a]	361–1066
^{103}Rh	−0.8468	21–374[a,d]	136–2427

[a] Goodfellow, R. J. In ref 5, pp 521–561. [b] Reference 6. [c] Benn, R.; Brenneke, H.; Joussen, E.; Lehmkuhl, H.; Ortiz, F. L. *Organometallics* **1990**, *9*, 756. [d] Reference 4.

Peaks due to the μ_4-$PPh(C_6H_4)$ group of **2** showed satellite peaks due to ^{101,99}Ru,^{31}P couplings, but they were not well resolved due to coupling to three nonequivalent ruthenium sites. Nevertheless, it is possible to estimate the largest coupling constant $^1J(^{101,99}\mathrm{Ru},^{31}\mathrm{P}) = 110$ Hz on the basis of the ^{31}P CP/MAS line widths.

The values obtained here for the one-bond ruthenium–phosphorus indirect spin–spin coupling constants can be compared with other transition metal phosphorus coupling constants by expressing them as reduced couplings:

$$K(\mathrm{M},^{31}\mathrm{P}) = (4\pi^2/h\gamma_M\gamma_P)J(\mathrm{M},^{31}\mathrm{P})$$

which are independent of the magnetogyric ratios (Table I). Clearly, the values of $K(^{99}\mathrm{Ru},^{31}\mathrm{P})$ are comparable to typical values of $K(^{57}\mathrm{Fe},^{31}\mathrm{P})$ and $K(^{187}\mathrm{Os},^{31}\mathrm{P})$.

In summary, we have demonstrated that indirect spin–spin coupling constants $J(^{101,99}\mathrm{Ru},^{31}\mathrm{P})$ can be obtained from ^{31}P CP/MAS NMR spectra of solid ruthenium phosphine complexes and measured the first values for J(Ru,P). These coupling constants and the residual dipolar interaction, d, are potentially powerful tools for probing structure and bonding in solid ruthenium complexes.

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(29) Typically, partial quadrupolar splittings are −0.43 to −0.55 for CO and −0.53 for PPh_3, while ligands involving other carbon multiple bonds exhibit more negative splittings, i.e. −0.84 for CN, −0.69 for CNR, or −0.96 mm/s for $CH_2{=}CH$.[30]

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