of methane was observed. After 2 h, the yellow solution was concentrated to ca. 10 mL and chilled to −20 °C to afford yellow crystals. Recrystallization from ether gave pure material: yield 71%; mp 89–91 °C.

Other alkyl(aryloxy)nickel(II) and -palladium(II) complexes were prepared analogously. Yields, melting points, elemental analyses, and IR and ^1H NMR spectral data are summarized in Table I.

Reactions of Alkylnickel and -palladium Complexes with CO. Complex **1f** (102 mg, 0.239 mmol) was dissolved in THF (2 mL). After evacuation, carbon monoxide (1 atm) was introduced. $MeCOOC_6H_4$-*p*-CN (0.197 mmol, 82%/Ni) was detected in the colorless solution after 1 day. The IR spectrum of the residual solid after volatiles were removed showed strong bands at 1910 and 1980 cm^{-1} attributable to $\nu(C{\equiv}O)$ of $Ni(CO)_2(PEt_3)_2$.[14]

Reactions of other alkylnickel and -palladium complexes are summarized in Table II.

Preparation of $Ni(COMe)(OC_6H_4$-*p*-$CN)(PEt_3)_2$, 3f. An equimolar amount of CO was introduced into a THF (5 mL) solution of **1f** (229 mg, 0.535 mmol) under vacuum at −78 °C, by using a mercury manometer. More than 90% of CO gas was absorbed in 6 h. After 10 h, the reaction was stopped and the yellow solid obtained by removing THF *in vacuo* was recrystallized from hexane to give air-sensitive yellow crystals: yield 22%; mp 80–83 °C dec. Elemental analysis was not feasible because of its high air sensitivity, and the complex was identified by IR and NMR spectroscopy: IR $\nu(C{\equiv}N)$ 2200 cm^{-1} (vs), $\nu(C{=}O)$ 1645 (vs), $\nu(C{-}O)$ 1340 cm^{-1}; ^1H NMR (benzene-d_6) NiCOMe, 2.55 ppm (s, 3 H), PEt_3, 1–2 ppm (m, 30 H), OC_6H_4-*p*-CN, 7.03 ppm (d, *J*(H–H) = 9Hz, 2 H), 7.35 (d, *J*(H–H) = 9Hz), 2 H).

Preparation of *trans*-$Pd(COMe)(OC_6H_4$-*p*-$CN)(PEt_3)_2$, 4e. Complex **2e** (661 mg, 1.39 mmol) in benzene (10 mL) was placed in an autoclave (50 mL) under nitrogen. CO gas (ca. 10 atm) was introduced into the autoclave. After the reaction system was stirred at room temperature for 5 h, the solution was transferred into a Schlenk type flask. Removal of solvent afforded a colorless solid which was recrystallized from ether to give colorless crystals: yield 50%; mp 54–55 °C; IR $\nu(C{\equiv}N)$ 2180 cm^{-1} (vs), $\nu(C{=}O)$ 1670 (vs); ^1H NMR (acetone-d_6) PdCOMe, 2.39 ppm (t, *J*(P–H) = 1 Hz, 3 H), PEt_3, 1.16 (qui, *J*(P–H) = *J*(H–H) = 8 Hz, 18 H), 1.60 (m, 12 H), OC_6H_4-*p*-CN, 6.72 (d, *J*(H–H) = 9 Hz, 2 H), 7.25 (d, *J*(H–H) = 9 Hz, 2 H). Anal. Calcd: C, 50.1; H, 7.4; N, 2.8. Found: C, 50.7; H, 7.4; N, 2.8. In this preparation starting material **2e** sometimes remained. Completion of the reaction was confirmed by monitoring the solution by ^1H NMR spectroscopy before performing isolation.

Registry No. **1a**, 72918-80-0; **1b**, 72918-78-6; **1c**, 72918-77-5; **1d**, 95910-33-1; **1e**, 79299-48-2; **1f**, 95841-39-7; **2a**, 95841-40-0; **2b**, 95841-41-1; **2c**, 95841-42-2; **2d**, 95841-43-3; **2e**, 95841-44-4; **2f**, 95841-45-5; **2g**, 95841-46-6; **3b**, 72918-83-3; **3c**, 72930-43-9; **3f**, 95841-47-7; **4e**, 95841-48-8; $Ni(CO)_2bpy$, 14917-14-7; $Ni(CO)_2(PEt_3)_2$, 16787-33-0; $Ni(AN)_2bpy$, 38566-75-5; Na_2IrCl_6, 16941-25-6; $NiMe_2(PEt_3)_2$, 60542-85-0; $PdMe_2bpy$, 95841-49-9; $PdMe_2(PEt_3)_2$, 29158-93-8; $PdMe_2(PMePh_2)_2$, 70354-76-6; $PdMe_2(PEtPh_2)_2$, 95910-34-2; AN, 107-13-1; MAnh, 108-31-6; dmpe, 23936-60-9; dpe, 1663-45-2; CH_3CO_2Ph, 122-79-2; $C_2H_5CO_2C_6H_4$-*p*-CN, 70978-62-0; $CH_3CO_2C_6H_4$-*p*-Ph, 148-86-7; $CH_3CO_2C_6H_4$-*p*-CN, 13031-41-9; $CH_3CO_2C_6H_4$-*p*-OMe, 1200-06-2; $CH_3CO_2C_6H_4$-*p*-Me, 140-39-6; HOC_6H_4-*p*-Me, 106-44-5; NCC_6H_4-*p*-OH, 767-00-0; $MeOC_6H_4$-*p*-OH, 150-76-5; C_6H_5OH, 108-95-2; CO, 630-08-0.

Communications

Intermediates in the Palladium-Catalyzed Reactions of 1,3-Dienes. 1. (η^3,η^3-Dodecatrienediyl)palladium, $[Pd(\eta^3,\eta^3\text{-}C_{12}H_{18})]$

R. Benn, P. W. Jolly,* R. Mynott, and G. Schenker[1]

Max-Planck-Institut für Kohlenforschung
D-4330 Mülheim a.d. Ruhr 1, West Germany

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Summary: Butadiene reacts with bis(dibenzylideneacetone)palladium to give the title compound. The NMR spectra indicate that the C_{12} chain in this molecule is arranged symmetrically around the palladium atom and has syn-substituted η^3-allyl groups and an uncomplexed cis double bond. Further reaction with bidentate ligands is accompanied by conversion of the η^3-allyl groups into the η^1-allyl form to give a 13-membered metallacycle. The significance of these complexes to the palladium-catalyzed linear trimerization of butadiene is discussed.

Although it has been known for over 20 years that donor ligand-free palladium catalysts convert butadiene into a mixture of isomers of the *linear* trimer dodecatetraene, there is little concrete information concerning the mechanism of this process. The original suggestion that an (η^2,η^3,η^3-dodecatriendiyl)palladium species,[2,3] related to the nickel complex isolated from the *cyclotrimerization* of butadiene,[4] is involved was abandoned in favor of a mechanism involving a binuclear species following the isolation of a complex of this type (eq 1) which was, moreover, shown to be an active catalyst for the linear trimerization of butadiene.[5-7] We report here evidence which implies that the original suggestion was essentially correct.

Bis(dibenzylideneacetone)palladium, $[Pd(dba)_2]$,[8] or the related bipyridine derivative [Pd(bpy)(dba)],[9] react with excess butadiene in ether at room temperature to give the

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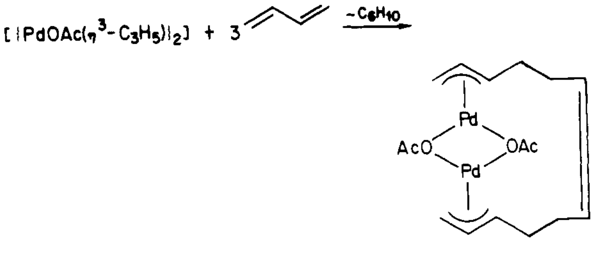
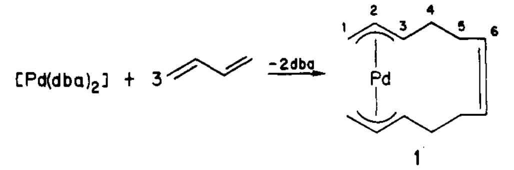


(1)

title compound 1 in ca. 30% isolated yield (the isolation is hampered by the catalytic formation of dodecatetraene) as a yellow, air-sensitive, crystalline compound which, in the absence of butadiene, decomposes at temperatures above −20 °C (eq 2).[10] The composition is established by the analytical data and mass spectrum, and the structure follows from the ^1H and ^{13}C NMR data[11] which indicate that the C_{12} chain is arranged symmetrically about the metal atom, that the η^3-allyl groups are syn substituted, and that the molecule contains an uncomplexed cis double bond. Below −80 °C, the six ^{13}C NMR signals become nondegenerate[11] suggesting either that, at these temperatures, the C_{12} chain adopts an unsymmetrical arrangement or, more probably, that two symmetrical conformations are frozen out.

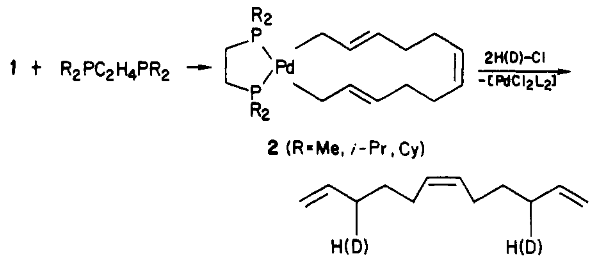


(2)

1

The configuration of the organic chain in 1 should be compared to that in the related complexes of nickel,[4] ruthenium,[13] molybdenum, and tungsten,[14] viz., [Ni(η^2,η^3,η^3-$C_{12}H_{18}$)], [$RuCl_2(\eta^2,\eta^3,\eta^3$-$C_{12}H_{18}$)] and [$M(CO)_2$($\eta^2,\eta^3,\eta^3$-$C_{12}H_{18}$)] (M = Mo, W), which have all been shown to contain a metal-bonded trans double bond and which differ in the anti (Ni) or syn (Ru, Mo, W) substitution of the allyl groups.

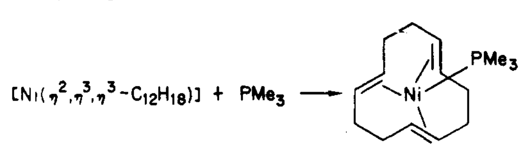
The reaction of 1 with bidentate bis(dialkylphosphino)ethanes in ether at −40 °C leads to the formation of the 13-membered palladacycles 2 as yellow to colorless compounds which decompose above −20 °C and which have been fully characterized (eq 3).[15] As far as we are aware, 2 is the largest known metallacycle. While the complexity of the ^1H NMR spectra prevented an unequivocable assignment of the cis double bond at C-6, its presence was confirmed by reaction of 2 with methanolic HCl: the only organic product isolated was *cis*-1,6,11-dodecatriene.



(3)

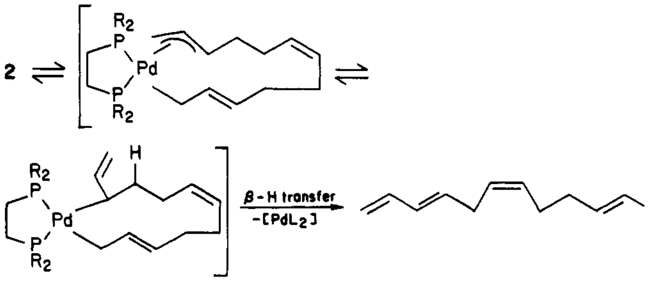
The relevance of 1 (and 2) to the mechanism of the palladium-catalyzed linear trimerization of butadiene is indicated by their reactions: the thermolysis (>−20 °C) as well as treatment with excess triphenylphosphine or carbon monoxide leads to the liberation of a mixture of dodecatetraene isomers. Hydrogenation of this mixture gives *n*-dodecane as the sole product.

This behavior toward donor ligands is in marked contrast to that of the related nickel complex [Ni(η^2,η^3,η^3-$C_{12}H_{18}$)] which reacts under ring closure to (*t,t,t*-cdt)Ni derivatives (eq 4)[4a,17] and is mirrored in the different behavior of the two metals in their catalytic reactions with butadiene strengthening the suggestion that complexes of the type described here are involved as intermediates in the catalytic processes.



(4)

The failure of the palladium complexes 1 and 2 to react with ring closure suggests that the C_{12} chain initially isomerizes to give an isomer having a vinyl substituent which then reacts further by the familiar β-H transfer (one variation is shown in eq 5). In this connection it should, however, be mentioned that ring closure has been observed on thermolysis of a nine-membered palladacyclic complex.[18]



(5)

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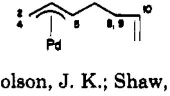
(10) [$Pd(dba)_2$] (3.1 g, 5.4 mmol) was suspended in ether (450 mL), and liquid butadiene (380 mL) was added at −20 °C. The reaction mixture was stirred for 75 min at room temperature and then cooled to −70 °C for 1.5 h and filtered at −10 °C. The yellow solution was evaporated to dryness at −30 °C and the resulting pale yellow solid taken up in pentane at −30 °C. The solution was filtered at −40 °C and evaporated to dryness. This process was repeated and the product finally dried under high vacuum for 1 day at −30 °C: yield 0.465 g (32% theory); MS (40 °C), *m/z* 268 (M^+), 214 ($M^+ - C_4H_6$), 160 ($M^+ - 2\ C_4H_6$), 106 ($M^+ - 3\ C_4H_6 = Pd^+$); IR (KBr, −35 °C) ν_{allyl} 1511 cm^{-1}, $\nu_{C=C(cis)}$ 1650 cm^{-1}. Anal. Calcd for $C_{12}H_{18}Pd$: C, 53.65; H, 6.75; Pd, 39.60. Found: C, 53.77; H, 6.82, Pd, 39.43.

(11) ^{13}C NMR (75.5 MHz, toluene-d_8, −30 °C) δ 46.6 (C-1), 115.1 (C-2), 82.1 (C-3), 33.1, 31.7 (C-4/C-5), 130.7 (C-6); ^{13}C NMR (75.5 MHz, THF-d_8 −100 °C) δ 47.7, 46.8, 115.9, 114.4, 83.1, 80.1, 34.9, 28.5, 33.4, 32.6, 131.1, 130.2; ^1H NMR (400 MHz, $CDCl_3$, −30 °C)[12] δ 4.88 (H-1, dt, $J_{1,2}$ = 7.3, $J_{1,4}$ = 13.0, $J_{1,5}$ = 12.4 Hz), 3.79 (H-2, d), 2.01 (H-4, d), 3.48 (H-5, m, $J_{5,6}$ = 4.4, $J_{5,7}$ = 10.8 Hz), 2.55, 1.84 (H-6/H-7, m, $J_{6,7}$ = −13.8, $J_{6,8}$ = 3.0, $J_{6,9}$ = 10.4, $J_{7,8}$ = 7.2, $J_{7,9}$ = 2.8 Hz), 2.39, 2.22 (H-8/H-9, m, $J_{8,9}$ = −13.0, $J_{8,10}$ = 4.7, $J_{9,10}$ = 7.6 Hz).

(12) Proton numbering scheme:



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(15) Anal. (R = Cy) Calcd for $C_{38}H_{66}P_2Pd$: C, 66.02; H, 9.02; P, 8.96; Pd, 15.39. Found: C, 66.16; H, 9.78; P, 8.83; Pd, 15.28. IR (KBr, −45 °C): $\nu_{C=C}$ 1630 cm^{-1}. NMR data (R = Me): ^{31}P NMR (32.4 MHz, THF-d_8, −40 °C) δ 18.8; ^{13}C NMR (75.5 MHz, THF-d_8, −30 °C) δ 28.6 (C-1, $J_{P,C}$ = ±97.7, ∓7.6 Hz), 138.3 (C-2, $J_{P,C}$ = ±8.9, ±2.3 Hz), 114.9 (C-3, $J_{P,C}$ = ±8.4, ±1.7 Hz), 33.4 (C-4), 28.9 (C-5), 131.3 (C-6), 11.9 (PMe), 27.9 (PCH_2), $J_{P,C}$ from analysis of the AA′X multiplet, $J_{P,P'}$ = 12.8 Hz; ^1H NMR (400 MHz, toluene-d_8, −40 °C)[16] δ 2.71 (H-1, d, $J_{1,2}$ = 8.7, $J_{1,P}$ = 18.2 Hz), 6.10 (H-2, dt, $J_{2,3}$ = 14.9 Hz), 5.63 (H-3, m, $J_{3,4}$ = 5.9 Hz), 2.46 (H-4/H-5, br, $J_{5,6}$ = 4.3 Hz), 5.49 (H-6, br, $J_{6,6'}$ = 10.7 Hz), 0.68 (PCH_2, d, $J_{H,P}$ = 15.6 Hz), 0.81 (PCH_3, d, $J_{H,P}$ = 7.9 Hz).

(16) Proton numbering scheme as for ^{13}C NMR spectrum.

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The lack of formation of dodecatriene having deuterium bonded to the terminal carbon atoms upon reaction of **2** with DCl (eq 3) apparently rules out a simple deuteriolysis of the Pd–C bond in this case. The deuterium in this reaction is found exclusively at C-3 and C-10 of the triene suggesting either that the reaction with acid is preceded by a rearrangement similar to that shown in eq 5 or, alternatively, that the acid attacks the allylic double bond directly.

Registry No. **1**, 96165-40-1; **2** (R = Me), 96193-93-0; **2** (R = *i*-Pr), 96165-41-2; **2** (R = Cy), 96165-42-3; $PdCl_2(Me_2PC_2H_4PMe_2)_2$, 15559-64-5; $PdCl_2((i\text{-}Pr)_2PC_2H_4P(Pr\text{-}i)_2)_2$, 96165-43-4; $PdCl_2(Cy_2PC_2H_4PCy_2)_2$, 96165-44-5; [Pd(dba)$_2$], 32005-36-0; [Pd(bpy)(dba)], 52462-56-3; $Me_2PC_2H_4PMe_2$, 23936-60-9; $(i\text{-}Pr)_2PC_2H_4P(i\text{-}Pr)_2$, 87532-69-2; $Cy_2PC_2H_4PCy_2$, 23743-26-2; *cis*-1,6,11-dodecatriene, 96165-45-6; butadiene, 106-99-0; dodecatetraene, 33637-94-4; *n*-dodecane, 112-40-3.

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Preparation, Structure, and Properties of Paramagnetic, Heterobinuclear Complexes Containing Nickel and Molybdenum or Tungsten. X-ray Crystal Structure of [NiW(CO)$_3$(PPh$_3$)$_2$(η-C$_5$H$_5$)]

Laurence Carlton, W. Edward Lindsell,* Kevin J. McCullough,* and Peter N. Preston

Chemistry Department, Heriot-Watt University
Riccarton, Edinburgh EH14 4AS, United Kingdom

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Summary: New paramagnetic complexes [MNi(CO)$_3$(PPh$_3$)$_2$(η-C$_5$H$_5$)] (M = Mo, W) have been characterized and studied by ESR spectroscopy, EHMO calculations, and cyclic voltammetry; the structure of crystalline [NiW(CO)$_3$(PPh$_3$)$_2$(η-C$_5$H$_5$)] has been determined by X-ray diffraction.

Current interest in heteronuclear derivatives containing both early and late transition metals[1,2] prompts us to report new, neutral, paramagnetic binuclear complexes of nickel with molybdenum or tungsten. Binuclear derivatives containing nickel bonded to a range of metals (e.g., Cr, Mo, W, Mn, Fe, Co)[1,3] are known, but these are all diamagnetic and mainly contain the entity Ni(η-C$_5$H$_5$). Also, the diamagnetic complexes [MnNi{μ-C(OMe)Ph}(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)][4] and [NiW$_2$(η-CC$_6$H$_4$Me-4)$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$][5] have been reported by Stone and co-workers. Several higher nuclearity heteroclusters containing nickel exist[1,6] including a few paramagnetic systems.[7] However, although the neutral d^9 Ni(I) complexes [NiXL$_3$] (L = phosphorus ligand) are well established,[8] the incorporation of such a center into a simple bimetallic complex has not been reported.

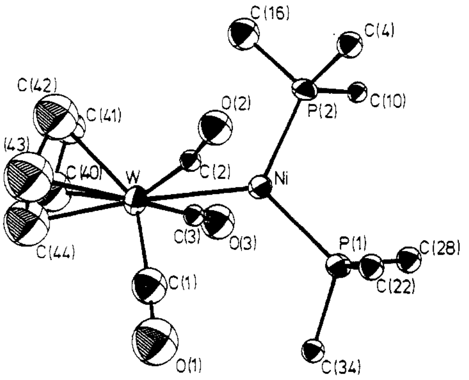

Figure 1. X-ray crystal structure of [NiW(CO)$_3$(PPh$_3$)$_2$(η^5-C$_5$H$_5$)] (**2**). Apart from the carbon atoms bonded to phosphorus, the remaining phenyl group carbons have been omitted for clarity. Some important geometrical parameters: W–Ni = 2.584 (3) Å, W–C(1) = 1.87 (3) Å, W–C(2) = 1.924 (20) Å, W–C(3) = 1.958 (21) Å, Ni–P(1) = 2.270 (7) Å, Ni–P(2) = 2.277 (7) Å, Ni–C(2) = 2.071 (20) Å, Ni–C(3) = 2.050 (21) Å; C(2)–W–C(3) = 103.2 (9)°, Ni–W–C(1) = 87.0 (9)°, Ni–W–C(2) = 52.2 (6)°, Ni–W–C(3) = 51.4 (6)°, W–Ni–P(1) = 121.01 (20)°, W–Ni–P(2) = 127.72 (19)°.

Reaction of Na[M(CO)$_3$(η-C$_5$H$_5$)] (M = Mo or W) with [NiCl$_2$(PPh$_3$)$_2$] in tetrahydrofuran at ambient temperature (2–10 min), followed by addition of water, filtration, and careful washing of the resulting solid with acetone gives crude product [MNi(CO)$_3$(PPh$_3$)$_2$(η-C$_5$H$_5$)], which may be recrystallized from dichloromethane–hexane {M = Mo (**1**), ca. 20%; M = W (**2**), 53%}. Both **1** and **2** form deep green crystals, moderately stable on short exposure to air but very air-sensitive in solution. In these syntheses Ni(II) is reduced to a formal Ni(0) state, although, with the heterometallic Ni–M bond, the Ni may be considered to be analogous to Ni(I) in complexes [NiXL$_n$]; other products isolated from the reaction mixtures include [M$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (M = Mo or W), [Ni(CO)$_2$(PPh$_3$)$_2$] (**3**) and [Ni{W(CO)$_3$(η-C$_5$H$_5$)}$_2$(PPh$_3$)$_2$] (**4**).[9]

The IR spectra[9] of **1** and **2** suggest the presence of bridging and terminal carbonyl groups. ^{1}H and ^{31}P NMR investigations of these complexes afforded either broad-

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[9] Anal. Calcd $C_{44}H_{35}O_3P_2MoNi$ (**1**): C, 63.80; H, 4.26; P, 7.48. Found: C, 63.69; H, 4.36; P, 7.56. Anal. Calcd $C_{44}H_{35}O_3P_2NiW$ (**2**): C, 57.68; H, 3.85; P, 6.76; Ni, 6.4; W, 20.1. Found: C, 57.51; H, 3.94; P, 6.61; Ni, 6.9; W, 20.9. Anal. Calcd $C_{52}H_{40}O_6P_2NiW_2$ (**4**): C, 50.0; H, 3.22. Found: C, 49.0; H, 3.45. IR spectra (ν(CO), cm^{-1}): (**1**) 1891, 1779, 1739 (Nujol); (**2**) 1895, 1770, 1730 (Nujol), 1892, 1769, 1741 (CH$_2$Cl$_2$); (**4**) 1935, 1917 (sh), 1870, 1840 (Nujol). ESR spectra (2-methyltetrahydrofuran, 10 °C): (**1**) g_{iso} = 2.118, $A_{iso}(^{31}P)$ = 7.49, 5.49 mT; (**2**) g_{iso} = 2.128, $A_{iso}(^{31}P)$ = 7.63, 5.89 mT.

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