(m, 2H); elemental analysis (%) calcd for $C_{14}H_{23}N_3CuCl_2O_8$: C 33.9, H 4.7, N 8.5; found: C 34.1, H 4.6, N 8.4.

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[11] Crystal data for **1**-$(ClO_4)_2$: STOE imaging plate diffraction system (IPDS) with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) equipped with an Oxford cryosystem cooling device operating at 180(2) K; φ scan method. Triclinic, $P\bar{1}$, $a = 8.0892(8)$, $b = 8.6971(8)$, $c = 13.9751(15)$ Å, $\alpha = 90.043(12)$, $\beta = 74.168(12)$, $\gamma = 67.401(11)°$, $V = 867.07(15)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.841\ Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 1.619\ mm^{-1}$, 3145 independent reflections; 306 parameters; $R = 0.0428$; $wR^2 = 0.1089$. Crystal data for **2**-$(ClO_4)_2$: Bruker CCD diffractometer, monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 298(2) K. Monoclinic, $P(2)1/n$, $a = 8.831(1)$, $b = 12.439(1)$, $c = 18.361(1)$ Å, $\beta = 93.1550(10)°$, $V = 2013.8(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.672\ mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 1.399\ mm^{-1}$, 4980 independent reflections; 267 parameters; $R = 0.0587$; $wR^2 = 0.1583$. CCDC 172506 and 172507 for **1** and **2**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[16] Parameters for the cyclic voltammetric measurements of **1**-$(ClO_4)_2$–**3**-$(ClO_4)_2$: scan rate of $100\ mV\,s^{-1}$, tetrabutylammonium hexafluorophosphate 0.2 M, CH_3CN, RT, potential reported relative to SSCE. Ferrocene was used as internal reference at $E_{1/2} = 370$ mV. **1**-$(ClO_4)_2$: irreversible reduction with a small returning wave, $E_{1/2} = -380$ mV, $E_{pc} = -445$ mV, $E_{pa} = -315$ mV, $\Delta E = 130$ mV. **2**-$(ClO_4)_2$: reversible wave at $E_{1/2} = -105$ mV, $E_{pc} = -145$ mV, $E_{pa} = -60$ mV, $\Delta E = 85$ mV. **3**-$(ClO_4)_2$: reversible wave at $E_{1/2} = -180$ mV, $E_{pc} = -240$ mV, $E_{pa} = -125$ mV, $\Delta E = 120$ mV.

[17] At 298 K, $[Cu^{II}L^1]_i = 1.25$ mM; $[L^1]_i/[Cu^{II}]_i = 1.28$; $[Cu^{II}L^2]_i = 1.21$ mM, $[L^2]_i/[Cu^{II}]_i = 1.28$.

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Migration of a Phosphane Ligand between the Two Metal Centers in Diruthenium Hydrido Complexes[**]

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In the coordination sphere of a metal cluster complex, the substrate can often interact with multiple metal centers simultaneously. The bridging coordination of hydride or carbon monoxide is a typical example of such interaction, and the multiple coordination of the ligand seems to be closely related to the dynamic behavior and reactivity of the ligand. Indeed, a carbonyl ligand in a cluster complex often undergoes intramolecular migration between the metal centers by way of an intermediary species with the bridging carbonyl.[1]For a better understanding of the nature of *multimetallic activation*, it is important to elucidate the interaction between the ligand and the multiple metal centers through the

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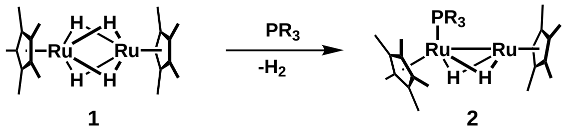
analysis of the molecular structure and the dynamic processes of the cluster complex.Previously, we reported that a bridging phosphido complex $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_6)]$ was formed in the reaction of $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}H)_4]$ (**1**)[2] with triphenylphosphane as a result of P–C(aromatic) bond cleavage induced by synergy of the adjacent metal centers.[3] We report herein the formation of novel dinuclear dihydrido complexes $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(PR_3)(\mu\text{-}H)_2]$ in the reaction of $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}H)_4]$ (**1**) with a phosphorus ligand containing no aryl substituents. We also discuss the intramolecular migration of the phosphorus ligand between the two ruthenium atoms.

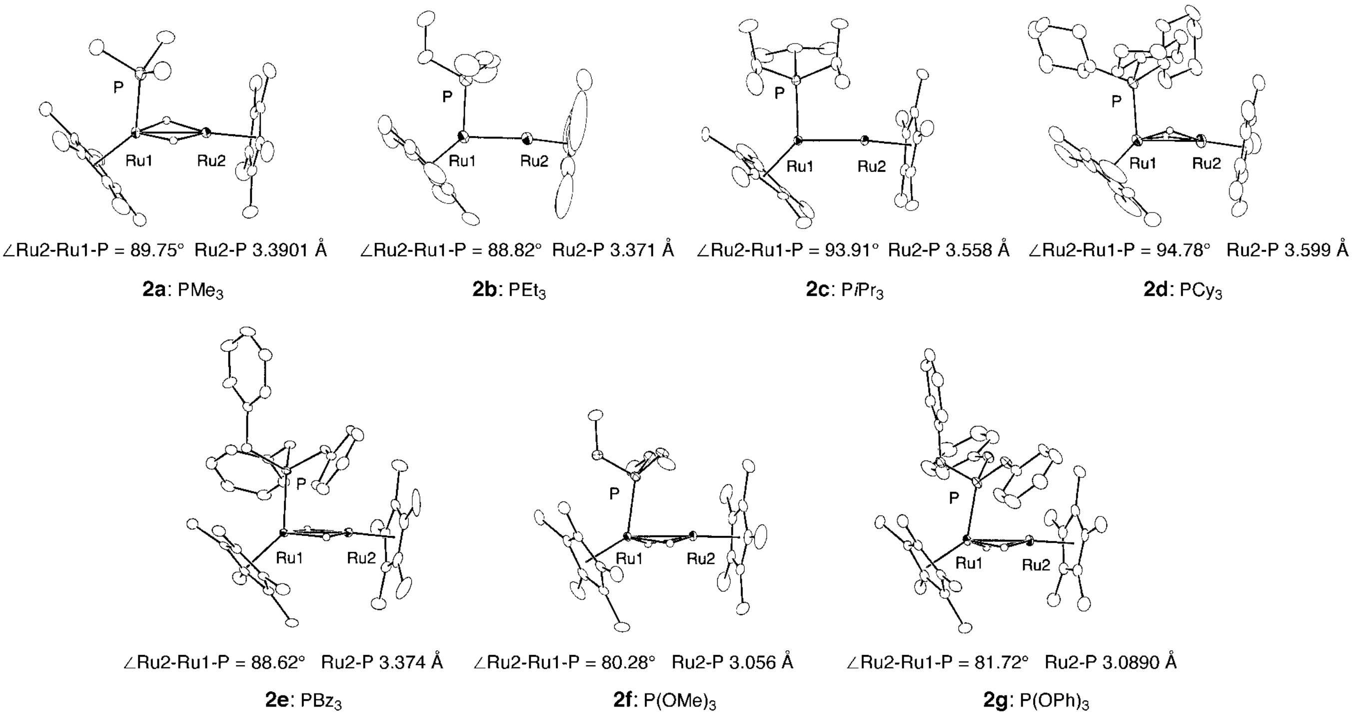
The reaction of **1** with an equimolar amount of a series of phosphorus ligands such as phosphanes and phosphites in toluene resulted in the quantitative formation of novel complexes $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(PR_3)(\mu\text{-}H)_2]$ (**2**) which bear the phosphorus ligand on one of the two ruthenium atoms [Eq. (1)]. Treatment of **2** with additional amounts of the phosphorus ligand does not yield the corresponding bisphosphane complexes, probably due to the steric hindrance to the incoming phosphorus ligand. Complexes **2a**–**2g** are highly unsaturated (30e) and sensitive to moisture and air. Selected spectral data of **2** are listed in Table 1. The ratio of integral intensities among the ^1H NMR signals for C_5Me_5, PR_3, and Ru-H of **2a**–**2g** indicated the formation of the dinuclear ruthenium dihydrido complexes containing a terminal phosphorus ligand. The ^{31}P NMR signals of **2a**–**2g** were observed in the range of $\delta = -7$ to 180 ppm. For example, the chemical shifts are $\delta = -6.9$, 77.9, 26.9, and 175.3 ppm for **2a**, **2c**, **2e**, and **2f**, respectively. These shifts are consistent with the coordination of the phosphorus ligands in the terminal mode.



1 **2** (1)

	2a	2b	2c	2d	2e	2f	2g
R	Me	Et	*i*Pr	Cy	Bz	OMe	OPh

The molecular structures of **2a**–**2g** were determined by X-ray diffraction studies.[4] The perspective views of the structures are shown in Figure 1, and the selected geometric parameters are listed in Table 1. The ORTEP drawings clearly show the unsymmetrical structure of **2** in each, with PR_3 terminally coordinated to one of the two ruthenium atoms. The Ru–Ru vector is almost perpendicular to the C_5Me_5 ligand coordinated to the Ru2. The Ru1 atom adopts an approximate piano-stool geometry. The Cp-Ru1-P1 angles are around 130° irrespective of the cone angle of the phosphorus ligands.[5] It is noteworthy that there is a significant correlation among the $\Sigma\chi_i$ values of PR_3,[5] the Ru1–P distances, and the Ru2-Ru1-P1 angle; with the increase of the electron-withdrawing character of the substituents on the phosphorus, the Ru1–P distance becomes shorter and the Ru2-Ru1-P1 angle narrows. Another notable feature of the structures is a short Ru–Ru distance (2.5084(4)–2.5502(7) Å) in agreement with the highly unsaturated (30e) character of **2**. A preliminary result of the DFT (B3LYP) calculation using a Gaussian98 A9 program package indicated that there was a direct bonding interaction between the two ruthenium atoms, which was less than that for a single bond;[6] however, the metal–metal bond is never a triple bond in accord with the EAN rule. The shortening the Ru–Ru bond is, therefore, probably due to the presence of bridging hydride.



∠Ru2-Ru1-P = 89.75° Ru2-P 3.3901 Å
2a: PMe_3

∠Ru2-Ru1-P = 88.82° Ru2-P 3.371 Å
2b: PEt_3

∠Ru2-Ru1-P = 93.91° Ru2-P 3.558 Å
2c: $P\textit{i}Pr_3$

∠Ru2-Ru1-P = 94.78° Ru2-P 3.599 Å
2d: PCy_3

∠Ru2-Ru1-P = 88.62° Ru2-P 3.374 Å
2e: PBz_3

∠Ru2-Ru1-P = 80.28° Ru2-P 3.056 Å
2f: $P(OMe)_3$

∠Ru2-Ru1-P = 81.72° Ru2-P 3.0890 Å
2g: $P(OPh)_3$

Figure 1. Molecular structures of **2a**–**2g**, with thermal ellipsoids at 30% probability level.

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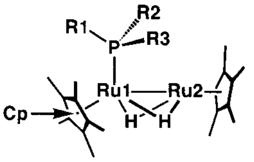
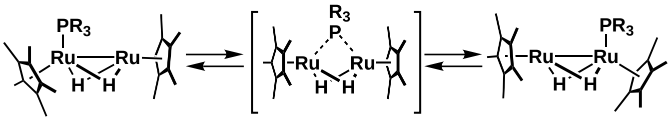
Table 1. Structural parameters and spectral data for complexes **2**.[a]



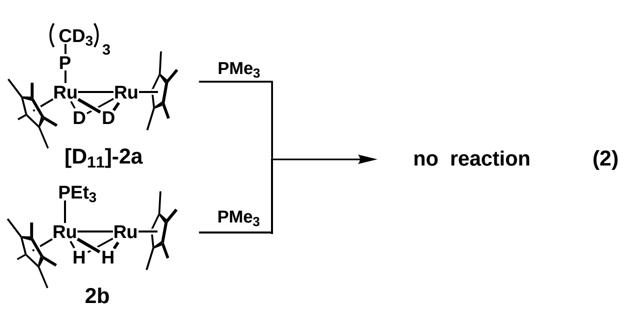
R	Me	Et	*i*Pr	Cy	Bz no. 1	 no. 2	OMe	OPh
Ru1−P distance	2.281(2)	2.285(2)	2.340(2)	2.336(2)	2.292(1)	2.299(1)	2.2175(9)	2.200(1)
P-Ru1-Cp angle	131.1	132.8	134.9	133.7	133.1	133.9	128.7	131.3
Ru2-Ru1-P angle	89.75(5)	88.82(6)	93.91(6)	94.78(4)	88.62(3)	86.16(3)	80.28(3)	81.72(3)
P-R1 distance	1.831(7)	1.845(8)	1.854(10)[b]	1.899(7)	1.880(4)	1.864(4)	1.625(2)	1.641(2)
P−R2, P−R3 distances	1.807(7)	1.81(1)	1.857(9)[b]	1.874(5)	1.860(4)	1.869(4)	1.616(2)	1.636(3)
	1.812(7)	1.846(9)	1.881(9)[b]	1.875(6)	1.847(4)	1.870(4)	1.611(2)	1.638(3)
Ru1−Ru2 distance	2.520(1)	2.5262(9)	2.5361(9)	2.5502(7)	2.5326(4)	2.5356(5)	2.5102(4)	2.5084(4)
$\Sigma\chi$i value[c]	7.8	5.6	3.1	0.3	10.3	10.3	23.4	29.2
Cone angle for PR3[c]	118	132	160	170	165	165	107	128
^{1}H NMR (C_5Me_5, δ, RT)[d]	1.88	1.87	1.71, 1.95	1.80, 2.00	1.75	1.75	1.90	1.77
^{1}H NMR (Ru−H, δ, RT)[d]	−13.65	−13.89	−14.75	−14.70	−13.44	−13.44	−14.23	−14.14
^{31}P{^{1}H} NMR (δ, RT)[d]	−6.89	36.3	77.9	64.9	26.9	26.9	175.3	147.1
$\Delta H^{\neq}_{\text{migration}}$ [kcal mol^{-1}]	6.8	9.2	12.6	15.7	7.2	7.2	6.2	–[e]
$\Delta S^{\neq}_{\text{migration}}$ [eu]	−8.0	−5.6	−8.8	−3.5	−16.3	−16.3	−14.0	–[e]

[a] Labeling scheme as shown. [b] P–R1 in **2c** does not stretch toward Ru2. [c] These values are cited in reference [5]. [d] In C_6D_6. [e] The activation parameters for **2g** could not be determined because the signals for C_5Me_5 groups are observed to be equivalent in the range from −110 °C to 25 °C.

Although the two cyclopentadienyl ligands in **2** are each in a different steric environment in the solid state, their ^{1}H NMR signals were observed to be equivalent above room temperature. As the temperature was lowered, the signal for the C_5Me_5 group was remarkably broadened and split into two peaks below about −100 °C. The intramolecular migration of the phosphorus ligand between the two ruthenium centers likely accounts for this fluxional behavior (Scheme 1). Only a few examples are thus far known for the migration of a terminal phosphane ligand among metal centers,[7] but the mechanistic details are still uncertain. The possibility of an intermolecular process, namely, liberation of the PR_3 group from one of the ruthenium centers and its recombination with another ruthenium atom, is ruled out because the coordinated PR_3 group in **2** is not exchanged with added phosphanes [Eq. (2)]. Kinetic parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, estimated from the line-shape analysis of the variable-temperature ^{1}H NMR spectra (Figure 2) are also listed in Table 1. The small $\Delta S^{\neq}$ values rule out the possibility of an intermolecular process, and are consistent with the above-mentioned intramolecular process. The values are similar to those found in migration of a



Scheme 1. Fluxional behavior of the diruthenium hydrido complexes.



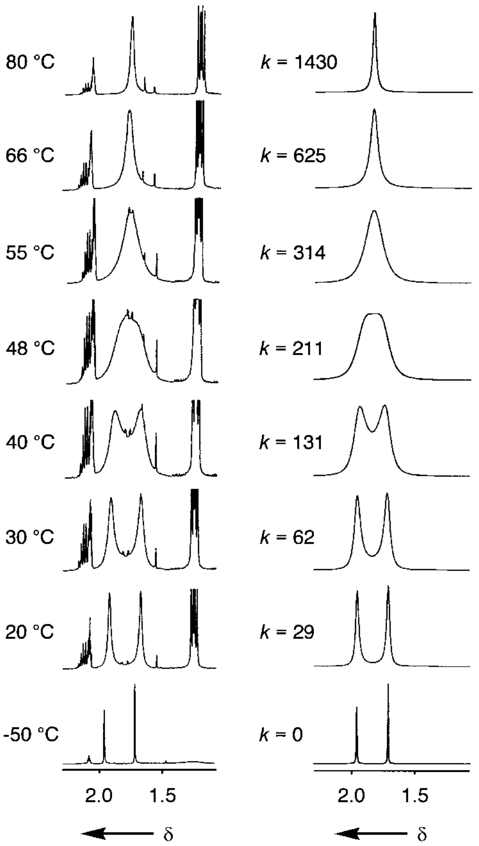


Figure 2. Variable-temperautre ^{1}H NMR spectra of **2c** (left) and calculated spectra (right; C_5Me_5 region).

silyl group on a diruthenium core.[8] A dinuclear species with a bridging five-coordinate phosphane ligand in between the two ruthenium atoms is plausible for the transition state (Scheme 1). Such a dinuclear μ-PR$_3$ complex has been reported recently,[9] and a dipalladium complex bridged by the pentacoordinate phosphane has also been reported.[10] There is a close correlation between the $\Delta H^{\ddagger}$ values and the electronic parameters $\Sigma\chi i$ defined by Tolman.[5] The more electron-withdrawing the substituent on the phosphane ligand is, the smaller the $\Delta H^{\ddagger}$ value is. This result suggests that through-space interaction between the phosphorus and Ru2, σ*(P–C)–d(Ru2) and/or p(P)–d(Ru2), possibly leads to the migration of the phosphorus ligand. Although we have not yet deduced which interaction is predominant, a linear relationship between the Ru2-Ru1-P angle and the $\Sigma\chi i$ value for the phosphorus ligand (Figure 3) is consistent with such a backbonding interaction. The enhancement of the Ru2–P backbonding interaction due to introduction of electron-withdrawing substituents on the phosphorus atom likely leads to the decrease of the Ru2-Ru1-P angle. The σ*(P–C)–d(Ru2) backbonding interaction may be rationalized by the coplanarity of the Ru2, Ru1, P, and R in **2a**, **2b**, **2f**, and **2g**, observed in the X-ray structure analyses.

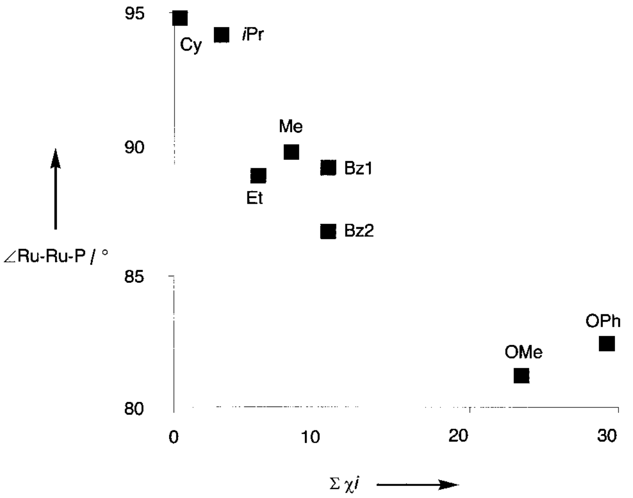


Figure 3. Relationship between Ru2-Ru1-P angles and electronic parameters $\Sigma\chi i$.

We have synthesized novel diruthenium complexes containing a phosphorus ligand and demonstrated the migration of the phosphorus ligand between the two ruthenium centers. From a thermodynamic and structural standpoint, we propose a through-space backbonding interaction between the ruthenium and phosphorus atoms.

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[1] For example, see: a) R. D. Adams, F. A. Cotton, *Dynamic Nuclear Magnetic Resonance Spectroscopy* (Eds.: L. Jackman, F. A. Cotton), Academic Press, New York, **1975**; b) E. L. Muetterties, E. Band, *Chem. Rev.* **1978**, *78*, 639–658; c) J. Evans, *Adv. Organomet. Chem.* **1977**, *16*, 319–347.

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[4] The diffraction data were measured on an AFC-7R four-circle diffractometer (**2a**, **2c**, **2f**) or RAXIS-2 imaging plate area detector (**2b**, **2d**, **2e**, **2g**). The structures were solved by the Patterson method (DIRDIF92 PATTY). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms except for Ru-H (refined isotropically) were fixed at the calculated positions. Crystal data for **2a**: monoclinic, $P2_1/n$, $a = 11.439(4)$, $b = 14.208(6)$, $c = 15.527(5)$ Å, $\beta = 90.79(3)°$, $V = 2523(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.450$ g cm^{-1}; 6316 reflections ($5° \leqq 2\theta \leqq 55°$), 4048 observed with $F > 3\sigma(F)$, 244 parameters; $R = 0.040$, $R_w = 0.037$. Crystal data for **2b**: monoclinic, $P2_1/c$, $a = 16.63(1)$, $b = 8.446(1)$, $c = 20.57(2)$ Å, $\beta = 95.00(7)°$, $V = 2878(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.368$ g cm^{-1}; 6646 reflections ($5° \leqq 2\theta \leqq 60°$), 4603 observed with $F > 3\sigma(F)$, 263 parameters; $R = 0.057$, $R_w = 0.054$. Crystal data for **2c**: monoclinic, Pn, $a = 11.168(4)$, $b = 11.170(4)$, $c = 11.902(4)$ Å, $\beta = 94.04(3)°$, $V = 1481.0(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.424$ g cm^{-1}; 3361 reflections ($5° \leqq 2\theta \leqq 55°$), 2859 observed with $F > 3\sigma(F)$, 290 parameters; $R = 0.038$, $R_w = 0.047$. Crystal data for **2d**: monoclinic, $P2_1/n$, $a = 30.8323(7)$, $b = 11.899(2)$, $c = 11.342(4)$ Å, $\beta = 91.27(2)°$, $V = 4159(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.321$ g cm^{-1}; 8667 reflections ($5° \leqq 2\theta \leqq 60°$), 5376 observed with $F > 3\sigma(F)$, 396 parameters; $R = 0.048$, $R_w = 0.060$. Crystal data for **2e**: triclinic, $P\bar{1}$, $a = 18.421(4)$, $b = 20.121(4)$, $c = 10.129(2)$ Å, $\alpha = 90.90(1)$, $\beta = 98.44(1)$, $\gamma = 88.19(2)°$, $V = 3711(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.394$ g cm^{-1}; 15623 reflections ($5° \leqq 2\theta \leqq 60°$), 11404 observed with $F > 3\sigma(F)$, 810 parameters; $R = 0.034$, $R_w = 0.033$. Crystal data for **2f**: monoclinic, $P2_1/n$, $a = 19.823(4)$, $b = 15.991(5)$, $c = 8.351(4)$ Å, $\beta = 98.86(3)°$, $V = 2615(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.520$ g cm^{-1}; 6638 reflections ($5° \leqq 2\theta \leqq 55°$), 4836 observed with $F > 3\sigma(F)$, 271 parameters; $R = 0.027$, $R_w = 0.025$. Crystal data for **2g**: monoclinic, $P2_1/a$, $a = 17.146(5)$, $b = 17.8115(9)$, $c = 11.599(2)$ Å, $\beta = 96.28(2)°$, $V = 3521.0(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.481$ g cm^{-1}; 7385 reflections ($5° \leqq 2\theta \leqq 60°$), 5970 observed with $F > 3\sigma(F)$, 406 parameters; $R = 0.037$, $R_w = 0.027$. CCDC-173306 to CCDC-173312 contains the supplementary crystallographic data (excluding stucture factors) for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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