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A convenient synthesis of bis(phosphino)methanes: Formation of a nickel(II) bis(phosphino)methane monoxide complex

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Abstract

The reaction of (trimethylsilyl)methyl phosphines $R_2PCH_2SiMe_3$ with chlorophosphines $CIPR'_2$ provides ready access to a range of symmetrical or non-symmetrical diphosphinomethanes $R_2PCH_2PR'_2$. The products are obtained cleanly and can be used directly in the synthesis of transition metal complexes. This is illustrated by the preparation and structural characterization of the corresponding NiCl₂(P–P) derivatives.

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1. Introduction

Bidentate phosphine ligands are widely used to stabilize transition metal complexes either in stable compounds or as intermediates in homogeneous catalysis [1]. There are currently many synthetic methods that provide access to a plethora of diphosphines, allowing precise tuning of the stereoelectronic properties of the metal center [2]. Bis(phosphino)methanes constitute a special group among these ligands, since their small bite angle results in a tendency to coordinate either in terminal η^1 mode or to bridge between two metal centres [3]. The presence of bulky groups on the phosphorus atoms [4] or alkyl substitution at the methylene group [5] increases the ligand preference to form chelated complexes, displaying strained four-membered MPCP cycles. In addition, the relatively acidic PCH₂P group can be easily deprotonated, rendering an anionic form of the ligands [6] and allowing the ready modification of the diphosphine backbone [7], a feature that contributes to further expand their rich coordination chemistry.

A number of synthetic methods have been devised to give access to bis(phosphino)methanes, but most of them are laborious or require the use of toxic or pyrophoric materials. Thus, the synthesis of symmetric R₂PCH₂PR₂ ligands usually relies on the alkylation of the dangerous and difficult to prepare tetrachlorodiphosphine Cl₂P-CH₂PCl₂ [8], or the reaction of alkali metal phosphides with dihalomethanes [2]. Hofmann has reported a versatile procedure, involving the reaction of the lithiated phosphines R₂PCH₂Li with PR₂'Cl, which allows the synthesis of several types of symmetric and unsymmetric $(R_2PCH_2PR'_2)$ ligands. A drawback of this method is the use of relatively large amounts of pyrophoric t-BuLi. In a safer modification of this strategy, developed by Werner, the lithiated R₂PCH₂Li reagent is prepared by reaction of the organotin derivatives R₂PCH₂SnPh₃ with *n*-BuLi under mild conditions. Interestingly, the organotin precursors can also react directly with chlorophosphines PR'₂Cl, to afford the desired diphosphines [9]. A similar condensation using less toxic organosilicon precursors was reported by Appel for the preparation of the diphosphines $PhP(R)CH_2PR_2$

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(R = Me, Ph) [10]. Herein, we describe the extension of the latter methodology for the synthesis of different ligands displaying the PCH₂P unit. A simple procedure has been developed, which minimizes the effort dedicated to the isolation and purification of intermediates. The ligands can be used as obtained for the preparation of metal complexes, and this is illustrated with the synthesis of several nickel derivatives, which have been structurally characterized.

2. Results and discussion

The synthesis of the bis(phosphino)methane derivatives 1-4 has been accomplished as shown in Scheme 1. Compounds 1 [10,11], 2 [10,12] and 4 [13] have been prepared before by different procedures, but 3 is described for the first time. Heating an equimolar mixture of the trimethylsilyl derivative R₂PCH₂SiMe₃ and the corresponding chlorophosphine without solvent at 250 °C for 20 min cleanly affords the diphosphines. The only byproduct, ClSiMe₃, is volatile and can be removed completely from the mixture at the end of the reaction by pumping at room temperature under reduced pressure. For the relatively small scale used in this work, the reaction can be safely conduced in a teflon-stopcock sealed 100 mL glass ampoule. However, for larger size preparations, a pressure reactor would be advisable, since the relatively volatile ClSiMe₃ may develop pressure. A conventional reflux apparatus has been avoided to prevent the contamination of the product by grease or by the action of ambient moisture. The starting trimethylsilylmethylphosphines [14] are also readily prepared from the reaction of commercially available Mg(CH₂SiMe₃)Cl with ClPR₂, and after hydrolysis and

drying with anhydrous MgSO₄, they are ready for use without any further purification.

An extension of this methodology allows the synthesis of polydentate ligands. Also shown in Scheme 1 is the reaction of the phosphine $P(CH_2SiMe_3)_3$ with $ClPPh_2$ under the above described reaction conditions, which cleanly affords the tetraphosphine **5**. The identity of the product is confirmed by its ${}^{31}P{}^{1}H{}$ spectrum, which shows an AX₃ spin system with a coupling constant of 100 Hz, similar to that of the diphosphines **2**–**4**. Only one more example of this type of CH₂-linked tetraphosphines is described in the literature, namely $P(CH_2PMe_2)_3$ [13b].

³¹P NMR monitoring indicates that all the condensation reactions proceed to completion and only one product is formed in an essentially quantitative manner. However, during the synthesis of **3**, it was observed the sublimation of a small amount of a white solid in the cold part of the reaction vessel. In spite of our efforts, we have been unable to ascertain the identity of this compound, which displays complex ³¹P and ¹H spectra. Notwithstanding this, this solid is easily removed, and the liquid phase is pure enough for synthetic purposes in all cases.

Ligands 1–3 react with NiCl₂ · 6(H₂O) in ethanol giving rise to the diamagnetic complexes 6–8. The ³¹P{¹H} spectrum of 6 consists of a singlet signal at δ –3.6 ppm, but those of the unsymmetric ligand derivatives 7 and 8 display strongly coupled AX spin systems with ²J_{PP} ≈ 200 Hz. The large value of the coupling constant is atypical for *cis* coordinated phosphorus atoms, and indicates an efficient transmission of the PP coupling either through the bridging carbon atom or the metal center, due to a significant departure from square planar geometry.



The crystal structures of the three compounds are shown in Fig. 1, and selected bond lengths and bond angles are listed in Table 1. The three compounds display distorted square planar structures. Their most prominent feature are the acute P-Ni-P angles of ca. 75°, while the Cl-Ni-Cl angles are somewhat wider than 90°. In contrast with NiCl₂(PCy₂CH₂PCy₂) [15], compounds 6-8 display negligible tetrahedral distortion. The Ni-P and Ni-Cl bond lengths of 7 are almost unaffected by the different nature of the R groups attached to the P atoms. Thus, the two Ni-Cl distances are almost identical within the experimental error, evincing that the different P donors exert comparable trans influence. However, in 8, the Ni-P(2) bond (2.1685(9) Å) is significantly longer than Ni–P(1) (2.1106(9) Å), probably due to the larger hindrance of the P'Pr₂ fragment as compared to the smaller PMe₂ unit. The steric origin of this effect is supported by the lack of a stronger trans influence of the latter group. In fact, the Ni-Cl2 bond, positioned trans to the presumably more strongly bound PMe₂ fragment, is slightly shorter (by ca. 0.03 Å) than Ni–Cl1.

The reaction of ligand 4 with $NiCl_2 \cdot 6(H_2O)$ follows a different course, and leads to the formation of the brown paramagnetic compound 9. Its crystal structure (Fig. 2) reveals that the bidentate ligand has undergone partial oxidation at the PMe₂ unit. The complex is binuclear, with the phosphine monoxide acting as a chelating ligand and bridging both metal centers through the oxygen atom. This is a very unusual feature, since only one example of structurally authenticated bridging coordination of a phosphine oxide has been reported previously [16]. The IR band associated to the P=O bond can be tentatively assigned to a medium intensity absorption at 1094 cm^{-1} . This frequency is somewhat lower than in structurally related complexes displaying terminal P=O coordination (ca. 1150 cm^{-1}) [17]. The nickel atoms are in a pseudooctahedral environment, which is completed by the two chloro ligands and a molecule of water. A planar ClPNi(µ-O)₂NiClP framework composes the core of the molecule. The P=O bridges are very symmetrical, with almost identical Ni-O bond distances (Ni-O1, 2.127(5) and Ni-O1A, 2.160(4) Å).

Table 1									
Selected 1	bond	distances ((Å) ar	nd bond	angles ((°) fc	or compo	unds (5-8

	6	7	8
Ni–P1	2.1407(5)	2.1451(6)	2.1106(9)
Ni–P2	2.1386(5)	2.1460(6)	2.1685(9)
Ni–Cl1	2.2091(5)	2.2068(6)	2.2293(9)
Ni-Cl2	2.2063(5)	2.2106(6)	2.1947(9)
P1–Ni–P2	75.366(19)	75.60(2)	75.03(3)
Cl1–Ni–Cl2	98.23(2)	96.82(2)	97.38(3)
P1C1P2	91.20(8)	91.41(10)	90.66(12)
TD^{a}	4.33(4)	3.64(2)	4.49(7)

^a Tetrahedral distortion, angle formed by planes P1–Ni–P2 and Cl1–Ni–Cl2.

The oxidation of coordinated phosphine ligands is not unusual, and it can involve intramolecular nucleophilic attack at the coordinated phosphorus atom [18]. Several diphosphine complexes of Ru and Pd undergo monooxidation by reaction with aqueous alkalis, with concomitant reduction of the metal center [19]. Based on this process, Grushin has developed a catalytic method for the selective



Fig. 2. Crystal structure of compound **9**. Selected bond distances (Å) and bond angles (°): Ni1–P1, 2.381(2); Ni1–O1, 2.161(4); Ni1–O1', 2.127(5); Ni1–O2, 2.077(5); Ni1–Cl1, 2.3438(17), Ni1–Cl2, 2.3924(18); P2–O1, 1.510(5) and P1–Ni1–O1, 84.59(13); Ni–O1–Ni1', 101.29(19); O1–Ni1–O1', 78.70(19); P1–C1–P2, 111.1(3).



Fig. 1. Crystal structure of compounds 6-8.



oxidation of diphosphines [17]. Since the reaction leading to compound **9** takes place under nitrogen atmosphere with careful exclusion of air, oxidation of the ligand by air seems unlikely. Therefore, we consider the water present in the starting hydrated nickel chloride as the most probable source of oxygen. As the oxidation state of Ni does not change along the process, water also acts as the final electron acceptor, releasing H₂. A possible mechanism for this reaction is shown in Scheme 2. The hydrolysis of a Ni–Cl bond generates a hydroxo ligand, which then attacks the coordinated P atom. The resulting nickel hydride reacts with the HCl generated by the hydrolysis, releasing hydrogen and giving rise to the NiCl₂ complex, which subsequently dimerizes to afford the final product.

3. Conclusions

Trimethylsilylmethyl phosphines react cleanly with chlorophosphines, providing a convenient method for the synthesis of different types of methylene bridged ligands, such as symmetrical and unsymmetrical diphosphinomethanes. The method can be extended to the preparation of polydentate ligands such as the tetraphosphine **5**. The reaction proceeds without solvent, and the ligands are directly obtained pure enough for synthetic purposes. This is demonstrated by the clean formation of the nickel complexes **6–8**, which have been structurally characterized. The reaction of hydrated nickel chloride with ligand **4** afforded the phosphine monoxide **9**, probably as a result of intramolecular attack of water to the coordinated phosphorus atom.

4. Experimental

All preparations and other operations were carried out under oxygen-free nitrogen atmosphere, using conventional Schlenk techniques. Diethyl ether and dichloromethane were dried and degassed before use. Absolute ethanol and the compounds PPh₂Cl, P^{*i*}Pr₂Cl were used as purchased. PMe₂Cl [20] and P(CH₂SiMe₃)₃ [21] were prepared according to literature methods. Microanalysis were performed by the Analytical Service of the Instituto de Investigaciones Químicas. NMR spectra were recorded using Bruker DPX-300, DRX-400 and DRX-500 spectrometers. The ¹³C and ¹H resonances of the solvent were used as an internal standard, and chemical shifts are reported with respect to SiMe₄. ³¹P chemical shifts are reported downfield of an external solution of H_3PO_4 (80%).

4.1. Synthesis of $R_2PCH_2SiMe_3$ ($R = {}^iPr$ [14a], Ph [14b])

19.8 mL of a 1.6 M solution of Mg(CH₂SiMe₃)Cl (31.4 mmol) were added dropwise to stirred solution of PR₂Cl (31.4 mmol) in diethyl ether, cooled to -80 °C. After stirring for 6 h at room temperature, a saturated solution of NH₄Cl was added. The mixture was decanted and the two layers were separated. The aqueous solution was washed with Et₂O (3 × 20 mL), and the washings combined with the organic phase. The resulting solution was dried with anhydrous MgSO₄, and the solvent removed under reduced pressure, affording the product as a colorless oil. ⁱPr₂PCH₂SiMe₃; Yield: 3.8 g (59%). ³¹P{¹H} NMR (C₆D₆, 25 °C): δ -5.0 ppm. Ph₂PCH₂SiMe₃; Yield: 6.6 g (77%). ³¹P{¹H} NMR (C₆D₆, 25 °C): δ -22.8 ppm.

4.2. Synthesis of diphosphines 1–4

Equimolar amounts (4 mmol) of $R_2PCH_2SiMe_3$ and $PCIR'_2$ were mixed in a 100 mL glass ampoule, sealed with a teflon stopcock, and heated with magnetic stirring at 250 °C for 20 min. The heating was confined to the lower part of the ampoule, to allow ClSiMe_3 to condense in the upper part. *Caution*. For larger scale preparations, a pressure reactor should be used. The mixture was cooled to room temperature and the ClSiMe_3 was evaporated in vacuo.

 ${}^{i}Pr_{2}PCH_{2}P^{i}Pr_{2}$ (1) [10,11]. Yield: 3.95 g (86%). ${}^{31}P{}^{1}H{}$ NMR (C₆D₆, 25 °C): δ -3.6 ppm.

^{*i*} $Pr_2PCH_2PPh_2$ (2) [10,12]. Yield: 1.06 g (84%). ³¹P{¹H} NMR (C₆D₆, 25 °C): δ -20.6 (d, ² J_{PP} = 117 Hz), -4.1 (d) ppm.

^{*i*}*Pr₂PCH₂PMe₂* (3). Quantitative yield. ¹H NMR (C₆D₆, 25 °C): δ 0.99 (d, 6H, ²*J*_{HP} = 3.0 Hz, P*Me*₂), 0.99 (partially hidden dd, 6H, ³*J*_{HH} = 7.0 Hz, ³*J*_{HP} = 1.1, CH *Me*Me), 1.04 (dd, 6H, ³*J*_{HH} = 7.0 Hz, ³*J*_{HP} = 4.2, CHMe*Me*), 1.19 (br d, 2H, ²*J* \approx 3.0 Hz, C*H*₂), 1.60 (sept d, 2H, CHMe₂) ppm. ¹³C{¹H} NMR (C₆D₆, 25 °C) δ = 15.8 (dd, ¹*J*_{CP} = 15 Hz, ³*J*_{CP} = 9 Hz, P*Me*₂), 18.6 (dd, ²*J*_{CP} = 10 Hz, ⁴*J*_{CP} = 2 Hz, CH *Me*Me), 19.8 (d, ²*J*_{CP} = 16 Hz, CHMe*Me*), 24.0 (dd, ¹*J*_{CP} = 15 Hz, ³*J*_{CP} = 6 Hz, CHMe₂), 24.4 (dd, ¹*J*_{CP} = 20 Hz, 32 Hz, CH₂) ppm. ³¹P{¹H} NMR (C₆D₆, 25 °C): δ -53.4 (d, ²*J*_{PP} = 98 Hz), -5.7 (d) ppm.

*Ph*₂*PCH*₂*PMe*₂ (4) [13]. Quantitative yield. ³¹P{¹H} NMR (C₆D₆, 25 °C): δ -53.3 (d, ²*J*_{PP} = 102 Hz), -20.5 (d) ppm.

4.3. Synthesis of $P(CH_2PPh_2)_3$ (5)

This compound was prepared as described for 1–4, from 0.73 g (2.5 mmol) of P(CH₂SiMe₃)₃ and 1.34 mL (7.5 mmol) of PPh₂Cl. Quantitative yield. ¹H NMR (C₆D₆, 25 °C): δ

2.42 (d, 6H, ${}^{2}J_{HP} = 1.9$ Hz, CH₂), 7.03 (m, 9H, C_{ar}H), 7.43 (m, 6H, $C_{ar}H$) ppm. ¹³C{¹H} NMR (C_6D_6 , 25 °C): δ 28.5 (m, CH_2), 128.8 (d, $J_{CP} = 6$ Hz, $C_{ar}H$), 128.9 (s, $C_{ar}H$), 133.5 (d, $J_{CP} = 19$ Hz, C_{ar} H), 140.0 (d, $J_{CP} = 15$ Hz, C_{ar}) ppm. ³¹P{¹H} NMR (C₆D₆, 25 °C): δ -36.5 (q, 1P, ²J_{PP} = 100 Hz), -25.2 (d, 3P, ²J_{PP} = 100 Hz) ppm.

4.4. Synthesis of complexes $NiCl_2(P-P)$ 6–8

A solution of 1 mmol of the appropriate diphosphine in 10 mL of anhydrous EtOH was added to a stirred solution of NiCl₂ \cdot 6H₂O (0.378 g, 1 mmol) in the same solvent. An immediate change of color from green to orange was observed. The mixture was stirred at room temperature for 1 h, and the solvent stripped to dryness. The orange residue was recrystallized from a minimum amount of dichloromethane.

 $NiCl_2({}^{i}Pr_2PCH_2P^{i}Pr_2)$ (6). Yield: 227 mg (60%). ¹H NMR (CD₂Cl₂, 25 °C): δ 1.38 (dd, 12H, ³*J*_{HH} = 7.1 Hz, ${}^{3}J_{\rm HP} = 8.5$ Hz, CH*Me*Me), 1.57 (dd, 12H, ${}^{3}J_{\rm HH} = 7.3$, ${}^{3}J_{HP} = 10.1$, CHMeMe), 2.11 (t, 2H, ${}^{2}J_{HP} = 19.1$ Hz, CH₂), 2.49 (m, 4H, CHMe₂) ppm. ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂, 25 °C): δ -15.7 ppm.

 $NiCl_2({}^{i}Pr_2CH_2PPh_2)$ (7). Yield: 370 mg (83%). Anal. Calc. for C₁₉H₂₆Cl₂P₂Ni: C, 51.2; H, 5.9. Found: C, 51.3; H, 5.9%. ¹H NMR (CD₂Cl₂, 25 °C): δ 1.26 (dd, 6H, ${}^{3}J_{\rm HP} = 17.0 \text{ Hz}, {}^{3}J_{\rm HH} = 6.8 \text{ Hz}, CH_{3}, 1.58 \text{ (dd, 6H, } {}^{3}J_{\rm HP}$ = 18.8 Hz, ${}^{3}J_{HH}$ = 6.9 Hz, CH₃), 2.34 (m, 2H, CH), 2.79 $(t, 2H, {}^{2}J_{HP} = 10.0 \text{ Hz}, CH_{2}), 7.55 \text{ (m, 4H, C}H_{ar}), 7.60 \text{ (m,}$ 2H, CH_{ar}), 8.16 (m, 4H, CH_{ar}) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 25 °C): δ 17.2 (s, CHMeMe), 18.8 (s, CHMeMe), 23.8 (dd, ${}^{1}J_{CP} = 29$ Hz, ${}^{1}J_{CP} = 21$ Hz, CH₂), 25.4 (d, ${}^{1}J_{CP} = 19$ Hz, CHMe₂), 127.7 (d, ${}^{1}J_{CP} = 41$ Hz, C_{ar}), 129.6 (d, $J_{CP} = 11$ Hz, CH_{ar}), 132.5 (d, $J_{CP} = 2$ Hz, CH_{ar}), 133.3 (d, $J_{CP} = 11$ Hz, CH_{ar}) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 25 °C): $\delta -51.7$ (d, ${}^{2}J_{PP} = 183$ Hz), -10.3 (d) ppm.

 $NiCl_2({}^{i}Pr_2CH_2PMe_2)$ (8). Yield: 997 mg (77%). Anal. Calc. for C₉H₂₂Cl₂P₂Ni: C, 33.6; H, 6.9. Found: C, 33.4; H, 6.7%. ¹H NMR (CD₂Cl₂, 25 °C): δ 1.39 (dd, 6H, ³J_{HP}) = 17.0 Hz, ${}^{3}J_{HH}$ = 7.8 Hz, CH *Me*Me), 1.63 (dd, 6H, ${}^{3}J_{HP}$ = 18.8 Hz, ${}^{3}J_{HH}$ = 7.0 Hz, CHMe *Me*), 1.71 (d, 6H, ${}^{2}J_{\text{HP}} = 13.3 \text{ Hz}, \text{ P}Me_{2}), 2.29 \text{ (4H, m, } CH + CH_{2}) \text{ ppm.}$ ¹³C{¹H} NMR (CD₂Cl₂, 25 °C): δ 13.1 (d, ¹J_{CP} = 26 Hz, PMe₂), 17.3 (s, CH MeMe), 18.7 (s, CHMeMe), 21.8 (dd, ${}^{1}J_{CP} = 28 \text{ Hz}, {}^{1}J_{CP} = 23 \text{ Hz}, CH_2), 24.4 \text{ (d, } {}^{1}J_{CP} = 17 \text{ Hz}, CHMe_2) \text{ ppm. } {}^{31}P{}^{1}H} \text{ NMR (CD}_2Cl_2, 25 ^{\circ}C): \delta -53.7$ $(d, {}^{2}J_{PP} = 201 \text{ Hz}), -14.3(d) \text{ ppm}.$

4.5. Synthesis of $[NiCl_2(H_2O)-\mu_2O-(Ph_2PCH_2P(O))]$ Me_2)- $\kappa P, O_2(9)$

0.24 g (1 mmol) of NiCl₂ \cdot 6H₂O, dissolved in 10 mL of EtOH was added to a stirred solution of Ph₂PCH₂PMe₂ (0.26 g, 1 mmol) in the same solvent. The color of the

Table 2

Crystallographic data collection, intensity measurements and structure refinement parameters for 6-9

	6	7	8	$9 \cdot 2CH_2Cl_2$
Chemical formula	C13H30Cl2NiP2	C19H26Cl2NiP2	C ₉ H ₂₂ Cl ₂ NiP ₂	C ₃₂ H ₄₀ Cl ₄ Ni ₂ O ₄ P ₄ , 2(CH ₂ Cl ₂)
FW	377.92	445.95	321.82	1017.57
$T\left(\mathbf{K}\right)$	100(2)	173(2)	173(2)	173(2)
Crystal size (mm)	$0.29 \times 0.25 \times 0.22$	$0.41 \times 0.14 \times 0.12$	$0.31 \times 0.20 \times 0.09$	$0.36 \times 0.34 \times 0.29$
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	Iba2	$P2_1/n$
a (Å)	13.3547(8)	11.2246(7)	13.5112(9)	11.6984(9)
b (Å)	10.6673(6)	15.2315(10)	13.8541(9)	14.3799(11)
c (Å)	14.3456(9)	12.5104(8)	16.0689(11)	12.7223(10)
α (°)	90	90	90	90
β (°)	116.312(1)	104.719(1)	90	98.329(2)
γ (°)	90	90	90	90
$V(\text{\AA}^3)$	1831.92(19)	2068.7(2)	3007.9(3)	2117.6(3)
Z	4	4	8	2
$\mu (\mathrm{mm}^{-1})$	1.510	1.350	1.825	1.580
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.370	1.432	1.421	1.596
<i>F</i> (000)	800	928	1344	1040
θ Range (°)	2.48-28.71	2.15-28.00	2.11-28.70	2.15-28.04
Number of measured reflections	16734	12265	9388	12438
Number of unique reflections $[R_{int}]$	4422 [0.0316]	4748 [0.0401]	3475 [0.0424]	4836 [0.0493]
Minimum and maximum transmission fact	0.6669 and 0.7373	0.3992 and 0.5252	0.6015 and 0.8529	0.6001 and 0.6572
Number of data/restraints/parameter	4422/0/283	4748/0/218	3475/1/133	4836/3/228
$R(F)(F^2 \ge 2\sigma(F^2))^a$	0.0307	0.0310	0.0303	0.0801
Observed reflections	3628	3212	2791	3202
$wR(F^2)$ [all data] ^b	0.0664	0.0524	0.0505	0.2423
Goodness-of-fit ^c [all data]	0.981	0.925	0.951	1.093
Absolute structure parameter ^d			0.016(14)	

 $R(F) = \sum ||F_0| - |F_c|| / \sum ||F_0|$ for 13567 11i (or 12034 12i) observed reflections.

 ${}^{b} wR(F^{2}) = \left(\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \right)^{1/2}.$ ${}^{c} \text{ Goodness-of-fit} = \left(\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \right)^{1/2}, \text{ where } n \text{ and } p \text{ are the number of data and parameters.}$

^d Ref. [23].

mixture changed from green to brown. After stirring for 1 h, the solvent was removed under reduced pressure. The brown residue was washed with Et₂O, and recrystallized from CH₂Cl₂. Yield: 466 mg (55%). FT-IR (Nujol mull): v 1094 cm⁻¹ (P=O).

4.6. X-ray crystal structure analyses of 6-9

A single crystal, of each representative compound (red block 6, orange block 7, orange prism 8 and green block $9 \cdot 2CH_2Cl_2$), of suitable size was mounted on a glass fiber using perfluoropolyether oil (FOMBLIN[®] 140/13, Aldrich). A summary of crystallographic data and structure refinement is reported in Table 2. Intensity data for 6 were collected on a Bruker-AXS SMART diffractometer/APEX CCD area detector, equipped with a graphite monocromated Mo Kal radiation ($\lambda = 0.71073$ Å) and a Bruker low-temperature device, whereas the data collections for complexes 7-9 were performed on a Siemens SMART 1 K diffractometer/CCD area detector, equipped with a graphite monochrotomator λ (Mo K α 1 radiation) = 0.71073 Å and an Oxford Cryosystem low-temperature device. The data collection strategy used in all the instance was ω rotations with narrow frames. Instrument and crystal stability were evaluated from the measurement of equivalent reflections at different measuring times and no decay was observed. The data were reduced using SAINT [22a] and corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied using SADABS [22b]. The structure was solved by direct methods using SIR-2002 [22c] and refined against all F^2 data by full-matrix leastsquares techniques using SHELXTL-6.12 [22d] minimizing $w[F_{0}^{2}-F_{c}^{2}]^{2}$. All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of compounds 7–9 were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters. For compound 6, the H atom positions were refined freely. Complete structural data have been deposited with CCDC Reference Nos. 286620(6), 286621 (7), 286622 (8) and 286623 (9).

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