Revised Supporting Information for **B817728G**

Facile Dichloromethane Activation and Phosphine Methylation. Isolation of Unprecedented Zwitterionic Organozinc and Organocobalt Intermediates

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Crystallographic data

X-ray data collection, structure solution and refinement for all compounds

Suitable crystals for the X-ray analysis of all compounds were obtained as described below. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer[S-1] (graphite monochromated MoK_α radiation, $\lambda = 0.71073$ Å). Crystallographic and experimental details for the structures are summarized in Tables S1 and S2. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[S-2] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms. In the crystals of **5**, a molecule of hexane was found disordered in proximity to the symmetry center. A satisfactory definition of the complete model was unsuccessful. A PLATON-SQUEEZE procedure[3] was run using the complete molecular model of compound **5**. The calculation (estimated residual electron density: 203 e/unit cell, total void volume in the unit cell: 560 $Å^3$) is consistent with the presence of 4 molecules of hexane. The modified reflection data were then used for the refinement of the molecular structure of **5**, resulting in improved refinement parameters. The ADDSYM algorithm of the package PLATON[3] detects an additional non-space group translation, resulting in the halving of the asymmetric unit in a **4**·$ZnCl_2$. The analysis and the refinement of the alternative model (featuring two slightly disordered orientations for each phenyls) induced us to discard this option, the missing operation being "*pseudo*". The non-metallated $ZnCl_2$ groups are disordered in two positions, having no atom in common. This, along with the poor quality of the crystals (resulting in a low observed/unique reflections ratio) lowers the structure quality. The model is in fact affected by a low C-C bond precision and poor anisotropic parameters, especially on the phenyls which are close to the disorder involving heavy atoms. CCDC 697021 $(PhPMe_3)_2(ZnCl_4)$, 697022 $(Ph_3PMe)[ZnCl_3(DMF)]$, 697023 $(Ph_3PMe)_2(ZnCl_4)$, 697024 $(Ph_3PMe)[ZnCl_3(H_2O)]$, 697025 (**5**·$1/2C_6H_{14}$), 697026 (**2_{ox}**), 697027 (**2_{th}**), 697028 (**4**), 697029 (**4**·$ZnCl_2$), 697030 $(Ph_3PMe)_2(Zn_2Cl_6)$ contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Data collection and refinement parameters for $(Ph_3PMe)_2(ZnCl_4)$, $(Ph_3PMe)_2(Zn_2Cl_6)$, $(Ph_3PMe)[ZnCl_3(DMF)]$ (DMF = dimethylformamide), $(Ph_3PMe)[ZnCl_3(H_2O)]$ and $(PhPMe_3)_2(Zn_2Cl_6)$.

Compound	$(Ph_3PMe)_2(ZnCl_4)$	$(Ph_3PMe)_2(Zn_2Cl_6)$	$(Ph_3PMe)[ZnCl_3(DMF)]$	$(Ph_3PMe)[ZnCl_3(H_2O)]$	$(PhPMe_3)_2(ZnCl_4)$
formula	$C_{38}H_{36}Cl_4P_2Zn$	$C_{38}H_{36}Cl_6P_2Zn_2$	$C_{22}H_{25}Cl_3NOPZn$	$C_{19}H_{20}Cl_3OPZn$	$C_{19}H_{29}Cl_7P_2Zn$
M_r	761.78	898.09	522.12	467.04	632.88
Cell setting,	Cubic,	Triclinic,	Monoclinic,	Monoclinic,	Monoclinic,
space group	$P2_13$	P-1	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	15.4168(6)	10.0538(3)	9.2816(4)	11.5221(5)	9.3861(3)
b (Å)	15.4168(6)	13.6096(4)	14.9139(4)	8.8570(2)	15.8823(8)
c (Å)	15.4168(6)	15.0143(4)	17.8177(7)	20.7669(5)	19.1608(9)
α (°)	90	91.832(2)	90	90	90
β (°)	90	102.291(2)	98.461(2)	94.549(2)	97.869(2)
γ (°)	90	98.875(2)	90	90	90
V (Å^3)	3664.4(2)	1978.8(1)	2439.7(2)	2112.6(1)	2829.4(2)
Z	4	2	4	4	4
D_x (Mg m^{-3})	1.381	1.507	1.421	1.468	1.485
μ (mm^{-1})	1.075	1.725	1.414	1.622	1.649
Crystal size (mm)	0.10×0.10×0.10	0.08×0.08×0.06	0.16×0.12×0.12	0.20×0.15×0.15	0.12x0.12x0.10
Meas, indep.,	2785, 2785,	12696, 9033,	14722, 5894,	12513, 4770,	11111, 6462,
obsvd. Refl.	2004	6746	4170	3508	4445
R_{int}	0.079	0.018	0.050	0.056	0.036
θ_{max} (°)	27.45	27.48	28.00	27.48	27.50
$R[F^2>2\sigma(F^2)]$,	0.046,	0.036,	0.037,	0.038,	0.038,
$wR[(F^2>2\sigma(F^2)]$,	0.081, 1.01	0.094, 1.07	0.081, 1.01	0.096, 1.06	0.067, 1.04
S					
parameters	138	435	265	235	378
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.739, -0.300	0.501, -0.712	0.347, -0.567	0.481, -0.689	0.409, -0.372
(e Å^{-3})					
Flack parameter	-0.02(2)				

Table S2: Data collection and refinement parameters for **4**, **4**·$ZnCl_2$, **5**·1/2C_6H_{14}, $\mathbf{2_{ox}}$ and $\mathbf{2_{th}}$.

Compound	**4**	**4**·$ZnCl_2$	**5**·1/2C_6H_{14}	$\mathbf{2_{ox}}$	$\mathbf{2_{th}}$
formula	$C_{38}H_{34}Cl_4P_2Zn_2$	$C_{76}H_{68}Cl_{12}P_4Zn_6$	$C_{37}H_{32}Cl_2CoP_2{\cdot}0.5(C_6H_{14})$	$C_{17}H_{19}Cl_3NOPZn$	$C_{17}H_{19}Cl_3NPSZn$
M_r	825.13	1922.80	668.45	456.02	472.08
Cell setting,	Monoclinic,	Triclinic,	Monoclinic,	Monoclinic,	Monoclinic,
space group	*C2/c*	*P*-1	*C2/c*	$P2_1/c$	$P2_1/c$
a (Å)	14.5489(7)	10.261(2)	24.424(1)	12.8862(3)	8.9222(2)
b (Å)	13.7296(3)	20.439(3)	12.4343(9)	8.4311(2)	17.2090(9)
c (Å)	18.8997(8)	21.995(3)	22.853(1)	18.2833(6)	13.8494(7)
α (°)	90	63.454(7)	90	90	90
β (°)	104.530(2)	86.058(9)	90.804(4)	98.131(1)	100.946(3)
γ (°)	90	83.865(8)	90	90	90
V (Å^3)	3654.5(2)	4101.8(11)	6939.7(7)	2439.73(16)	2087.8(2)
Z	4	2	8	4	4
D_x (Mg m^{-3})	1.500	1.557	1.279	1.540	1.502
μ (mm^{-1})	1.720	2.236	0.769	1.742	1.736
Crystal size (mm)	0.12×0.12×0.10	0.10×0.08×0.06	0.06x0.04x0.02	0.10×0.10×0.08	0.12×0.12×0.08
Meas, indep.,	12656, 5318,	20257, 14092,	10466, 6128,	8557, 4749,	7536, 4340,
obsvd. Refl.	3964	5537	3170	3158	2911
R_{int}	0.043	0.056	0.060	0.043	0.029
θ_{max} (°)	30.03	25.05	25.05	28.00	26.50
R [$F^2 > 2\sigma(F^2)$],	0.035,	0.086,	0.075,	0.040,	0.036,
wR[$(F^2>2\sigma(F^2)$], S	0.089, 1.05	0.183, 0.98	0.206, 1.01	0.084, 1.00	0.092,0.99
parameters	208	939	379	218	218
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.484, -0.854	0.516, -0.617	0.452, -0702	0.478, -0.607	0.315, -0.323

The crystal structures of the phosphoniums salts $(Ph_3PCH_3)_2(ZnCl_4)$, $(Ph_3PCH_3)_2(Zn_2Cl_6)$, $(Ph_3PCH_3)[ZnCl_3(DMF)]$ (DMF = dimethylformamide), $(Ph_3PCH_3)[ZnCl_3(H_2O)]$ and $(PhPMe_3)_2(ZnCl_4)$ were determined by single crystal X-ray diffraction. Their ORTEP plots are reported in Figures S1-S5. An ORTEP plot of the molecular structure of $\mathbf{2_{th}}$ is reported in Figure S6.

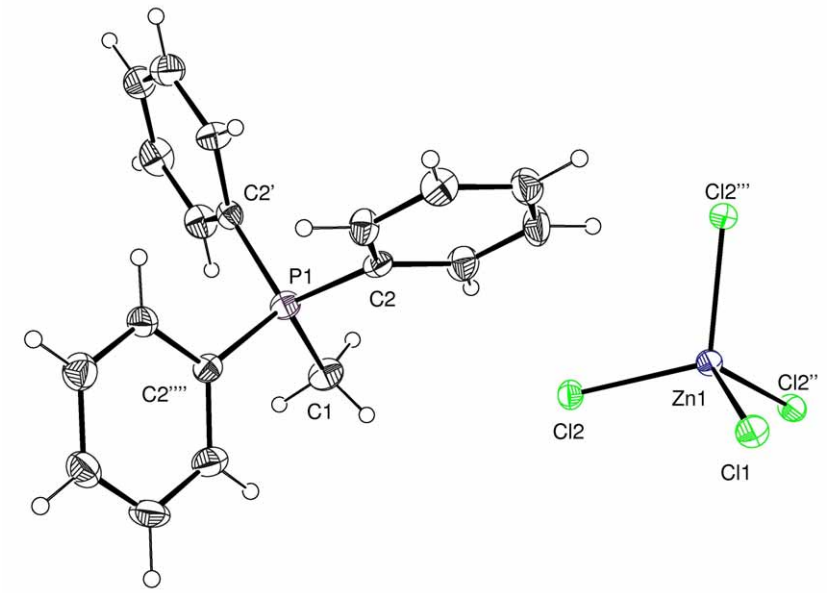


Figure S1. ORTEP view of the molecular structure of $(Ph_3PCH_3)_2(ZnCl_4)$. Ellipsoids at 50% probability level. Only one of the two independent phosphonium cations is depicted. Symmetry operations used to generate equivalent atoms: -1/2+y, 1/2-z, -x (′′′), -z, 1/2+x, 1/2-y (′′), -1/2+z, 1/2-x, 1-y (′) and 1/2-y, 1-z, 1/2 +x (′′′′).

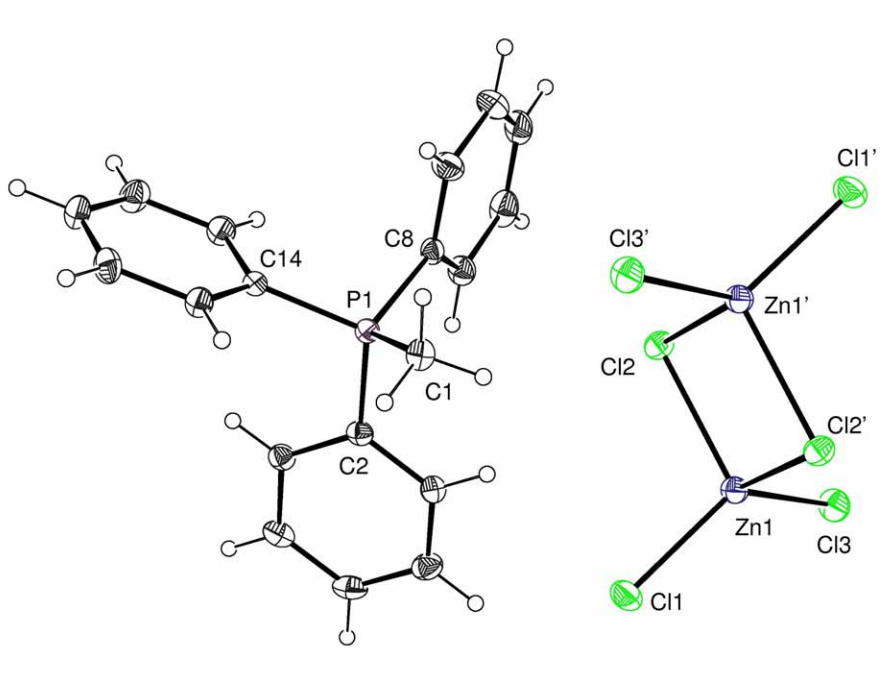


Figure S2. ORTEP view of the molecular structure of $(Ph_3PCH_3)_2(Zn_2Cl_6)$. Ellipsoids at 50% probability level. Only one of the two independent phosphonium cation is depicted. Symmetry operation used to generate equivalent atoms: -x, -y, -z (′).

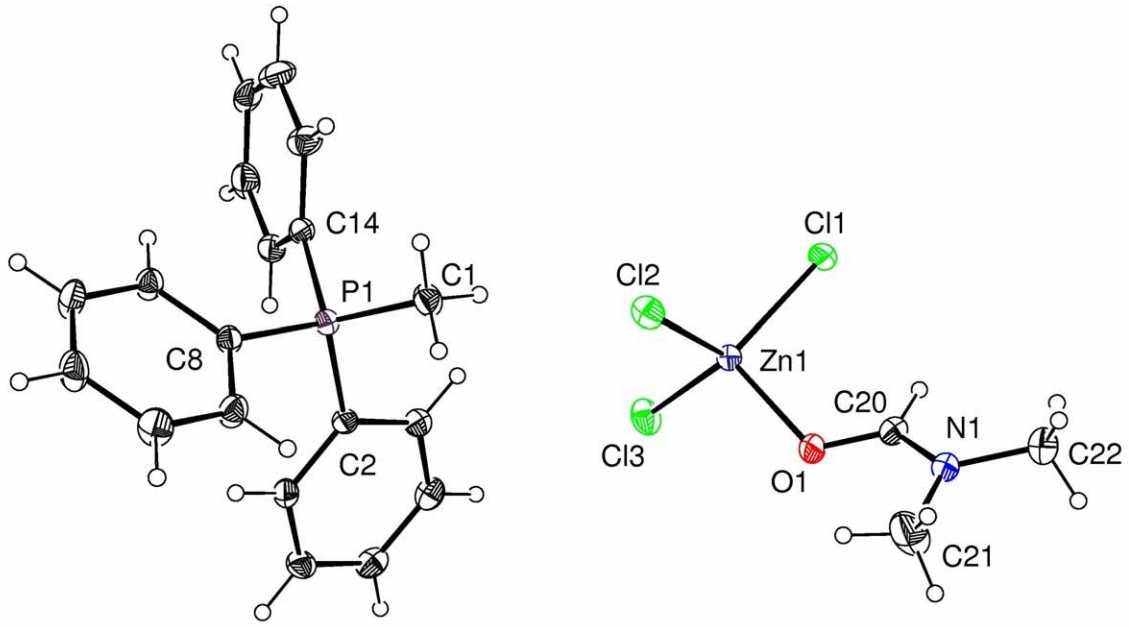


Figure S3. ORTEP view of the molecular structure of $(Ph_3PCH_3)[ZnCl_3(DMF)]$. Ellipsoids at 50% probability level.

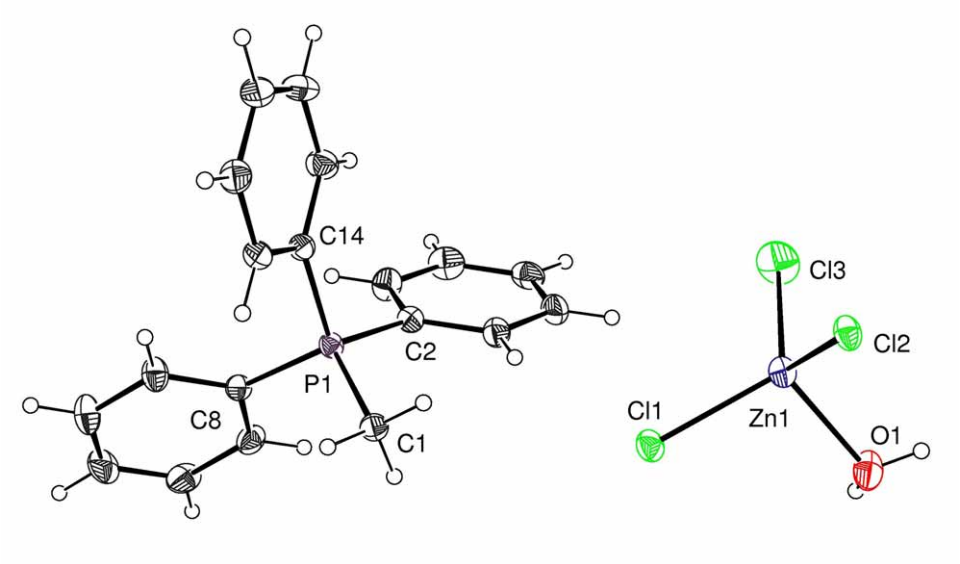


Figure S4. ORTEP view of the molecular structure of $(Ph_3PCH_3)[ZnCl_3(H_2O)]$. Ellipsoids at 50% probability level.

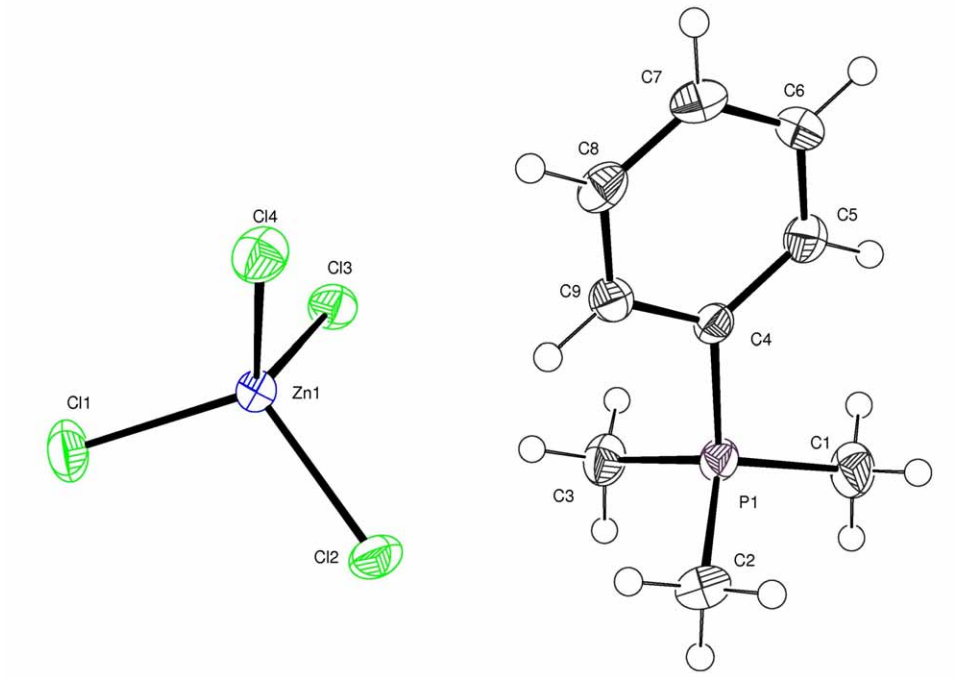


Figure S5. ORTEP view of the molecular structure of $(PhPMe_3)_2(ZnCl_4)$. Ellipsoids at 50% probability level. Only one of the two independent phosphonium cations is reported.

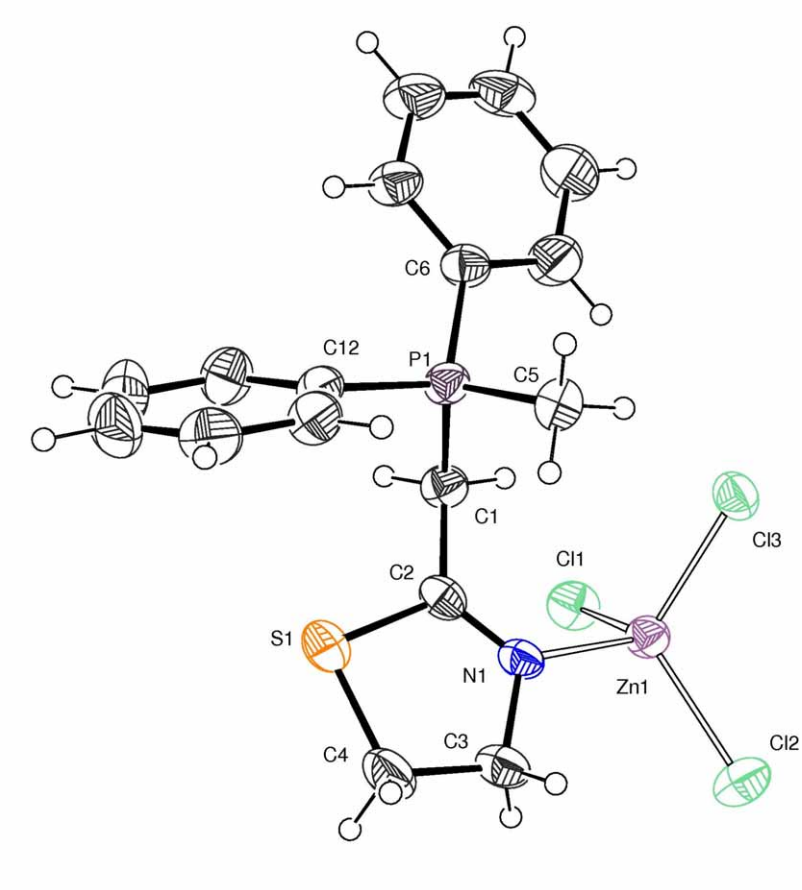


Figure S6. ORTEP view of the molecular structure of $\mathbf{2_{th}}$. Ellipsoids at 50% probability level.

Synthesis data

General Considerations

All manipulations were carried out under inert dinitrogen atmosphere, using standard Schlenk-line conditions and dried and freshly distilled solvents. The ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded unless otherwise stated on a Bruker Avance 300 instrument at 300.13, 75.48 and 121.49 MHz, respectively, using TMS, or H_3PO_4 (85% in D_2O) as external standards with downfield shifts reported as positive. FT-IR spectra in the range of 4000–650 cm^{-1} were recorded on a Thermo Nicolet 6700 instrument, equipped with SMART Orbit Diamond ATR accessory. Elemental C, H, N analyses were performed by the "Service de microanalyses",

Université Louis Pasteur, Strasbourg. The ligands 2-[(diphenylphosphino)methyl]oxazoline ($\mathbf{1_{ox}}$)[S-4] and 2-[(diphenylphosphino)methyl]thiazoline ($\mathbf{1_{th}}$)[S-5] were prepared according to literature procedures. Other chemicals were commercially available and used as received.

Zwitterion-salt equilibrium for $\mathbf{2_{ox}}$ and $\mathbf{2_{th}}$

In solution, a zwitterion-salt equilibrium was observed by variable temperature ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR (Scheme S1) for $\mathbf{2_{ox}}$ and $\mathbf{2_{th}}$. At room temperature, this equilibrium is shifted to the left for $\mathbf{2_{ox}}$ and to the right for $\mathbf{2_{th}}$. The corresponding enamino tautomer of $\mathbf{1_{ox}}$ has been previously postulated on the basis of its reactivity towards Ph_2PCl.[S-6]

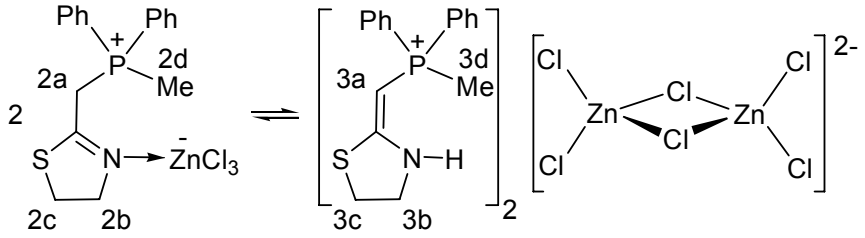
Preparation of $\mathbf{2_{ox}}$/$\mathbf{3_{ox}}$

Solid $\mathbf{1_{ox}}$ (0.066 g, 0.25 mmol) was added to a suspension of anhydrous $CoCl_2$ (0.032 g, 0.25 mmol) in dichloromethane (15 mL). The solution was stirred for 20 min. and zinc powder (0.250 g, 3.85 mmol) was added. The deep blue suspension was stirred at room temperature for 2 days, giving rise to a colourless solution which was filtered. Diethyl ether was layered onto the solution, affording colourless crystals of $\mathbf{2_{ox}}$ (0.092 g, yield = 82.2%). FT-IR ($\nu_{C=N}$): 1660 cm^{-1}. $\mathbf{2_{ox}}$: ^{1}H NMR (300.13 MHz, d_6-DMSO): δ = 2.80 (d, 3H, $^{2}J_{P-H}$ = 14.8 Hz, PCH_3), 3.69 (t, 2H, $^{3}J_{H-H}$ = 9.5 Hz, NCH_2), 4.15 (t, 2 H, $^{3}J_{H-H}$ = 9.5 Hz, OCH_2), 4.51 (d, 2H, $^{2}J_{P-H}$ = 15.6 Hz, PCH_2), 7.58–7.98 (m, 10 H, phenyls) ppm. ^{31}P{^{1}H} (121.5 MHz, d_6-DMSO): δ = 23.5 (s) ppm. ^{13}C{^{1}H} (75.48 MHz, d_6-DMSO): 6.9 (d, $^{1}J_{P-C}$ = 54.5 Hz, PCH_3), 22.8 (d, $^{1}J_{P-C}$ = 57.4 Hz, PCH_2), 54.6 (s, NCH_2), 68.5 (s, OCH_2), 119.8 –135.1 (m, phenyls), 160.8 (br, O-C=N) ppm. ^{31}P{^{1}H} (121.49 MHz, CD_2Cl_2): δ = 23.0 (s) ppm. $\mathbf{3_{ox}}$: ^{1}H NMR (300.13 MHz, d_6-DMSO): δ = 2.47 (d, 3H, $^{2}J_{P-H}$ = 14.1 Hz, PCH_3), 3.37 (d, 1H, $^{2}J_{P-H}$ = 11.8 Hz, PCH), 3.61 (t, 2H, $^{3}J_{H-H}$ = 7.9 Hz, NCH_2), 4.40 (t, 2H, $^{3}J_{H-H}$ = 7.9 Hz, OCH_2), 7.65–7.76 (m, 10 H, phenyls), 8.83 (s, br, 1H, NH) ppm. ^{13}C{^{1}H} (75.48 MHz, d_6-DMSO): δ = 11.2 (d, $^{1}J_{P-C}$ = 62.8 Hz, PCH_3), 35.9 (d, $^{1}J_{P-C}$ = 121.4 Hz, PCH), 43.1 (s, NCH_2), 70.5 (s, OCH_2), 119.8–135.1 (m, phenyls), 169.5 (s, O-C-NH) ppm. ^{31}P{^{1}H} (121.49 MHz, d_6-DMSO): δ = 14.4 (s) ppm. Anal. Calcd for $C_{17}H_{19}Cl_3NOPZn$ (456.06): C, 44.77; H, 4.20; N, 3.07. Found: C, 44.75; H, 4.12; N, 3.01.

Preparation of $\mathbf{2_{th}}$/$\mathbf{3_{th}}$

Solid $\mathbf{1_{th}}$ (0.286 g, 1.00 mmol) was added to a suspension of anhydrous $CoCl_2$ (0.065 g, 0.50

mmol) in dichloromethane (20 mL) and zinc powder (0.163 g, 2.51 mmol) was added. The deep blue suspension was stirred at room temperature for 2 days giving rise to a pale brown solution which was filtered. Evaporation of the volatiles yielded a brown solid which was washed with Et_2O (3 x 30 mL). Evaporation of the volatiles gave $\mathbf{2_{th}}$ as a colourless powder (yield: 0.347 g, 73.3%). Complex $\mathbf{2_{th}}$ can be recrystallized from a saturated CH_2Cl_2 solution. FT-IR ($\nu_{C=N}$): 1593 cm^{-1}. $\mathbf{2_{th}}$: ^{1}H NMR (300.13 MHz, d_6-DMSO): δ = 2.78 (d, 3H, $^2J_{P-H}$ = 14.8 Hz, PCH_3), 3.33 (t, 2H, $^3J_{H-H}$ = 8.4 Hz, SCH_2), 4.06 (t, 2H, $^3J_{H-H}$ = 8.4 Hz, NCH_2), 4.72 (d, 2H, $^2J_{P-H}$ = 15.1 Hz, PCH_2), 7.50–7.94 (m, 10H, phenyls) ppm. $^{13}C\{^1H\}$ (75.48 MHz, d_6-DMSO): δ = 7.2 (d, $^1J_{P-C}$ = 55.1 Hz, PCH_3), 27.2 (d, $^1J_{P-C}$ = 53.9 Hz, PCH_2), 34.7 (s, SCH_2), 65.0 (s, NCH_2), 120–135 (m, phenyls), 160.8 (d, $^2J_{P-C}$ = 8.0 Hz, S-C=N) ppm. $^{31}P\{^1H\}$ (121.49 MHz, d_6-DMSO): δ = 24.0 (s) ppm. $\mathbf{3_{th}}$: ^{1}H NMR (300.13 MHz, d_6-DMSO): δ = 2.54 (d, partially masked by DMSO, 3H, $^2J_{P-H} \approx$ 14 Hz, PCH_3), 3.26 (t, 2H, $^3J_{H-H}$ = 6.9 Hz, SCH_2), 3.64 (t, 2H, $^3J_{H-H}$ = 6.9 Hz, NCH_2), 4.37 (d, 1H, $^2J_{P-H}$ = 13.2 Hz, PCH), 7.50–7.94 (m, 10H, phenyls), 8.83 (s, br, 1H, NH) ppm. $^{13}C\{^1H\}$ (75.48 MHz, d_6-DMSO): δ = 11.2 (d, $^1J_{P-C}$ = 62.5 Hz, PCH_3), 32.7 (s, SCH_2), 48.5 (s, NCH_2), 54.4 (d, $^1J_{P-C}$ = 121.2 Hz, PCH), 120–135 (m, phenyls), 170.7 (d, $^2J_{P-C}$ = 9.7 Hz, S-C-NH) ppm. $^{31}P\{^1H\}$ (121.49 MHz, d_6-DMSO): δ = 15.2 (s) ppm. Anal. Calcd for $C_{17}H_{19}Cl_3NPSZn$ (472.13): C, 43.25; H, 4.06; N, 2.97. Found: C, 43.28; H, 4.11; N, 2.95. ^{1}H NMR spectra at variable temperatures are reported in Figure S6. The labeling scheme is given in Scheme S1.



Scheme S1.

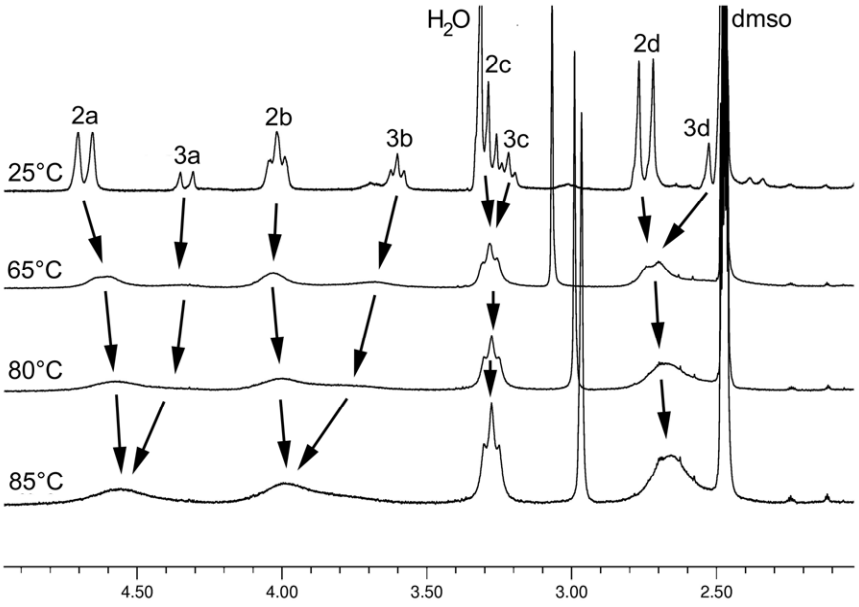


Figure S-6. Variable Temperature ^{1}H NMR spectrum of $\mathbf{2_{ox}/3_{ox}}$ in d_6-DMSO (see labeling in Scheme S1)

General procedure for the synthesis of $[Ph_{3-n}PMe_{n+1}]_2(ZnCl_4)$ (n = 0, 1 or 2).

To a suspension of anhydrous $CoCl_2$ (0.100 g, 0.77 mmol) in CH_2Cl_2 (15 mL) was added PR'R_2 (1.54 mmol, 0.403 g for R = R′ = Ph, 0.308 g for R = Ph, R′ = Me, 0.213 g for R = Me, R′ = Ph). The suspension was stirred for 20 min, giving rise to a deep blue suspension to which Zn powder was added (0.325 g, 5.00 mmol). The reaction mixture was stirred until discoloration (12 h). Dichloromethane (50 mL) was added and the solution was filtered. Distilled water was added (50 mL) to this solution A, the suspension stirred for 1 h and the organic part was collected. After drying with Na_2SO_4, the volatiles were removed under vacuum giving $[Ph_{3-n}P(CH_3)_{n+1}]_2(ZnCl_4)$ as colourless powders. Yields, based on phosphorus: (1.34 mmol, 0.451 g for R = R′ = Ph (87%); 1.43 mmol, 0.456 g for R = Ph, R′ = Me (92%); 1.20, 0.308 g for R = Me, R′ = Ph (78%). Crystals of $(Ph_3PMe)_2(Zn_2Cl_6)$ were obtained by addition of 2M HCl instead of water to solution A, while $(Ph_3PMe)[ZnCl_3(DMF)]$ was obtained by layering Et_2O onto a DMF solution of $(Ph_3PMe)_2(Zn_2Cl_6)$.

$(Ph_3PMe)_2(ZnCl_4)$: ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 3.21 (d, 6H, $^{2}J_{P–H}$ = 13.0 Hz, PCH_3), 7.68–7.87 (m, 30 H, phenyls) ppm. $^{13}C\{^{1}H\}$ (75.48 MHz, CD_2Cl_2): δ = 10.5 (d, $^{1}J_{P–C}$ = 56.7 Hz, PCH_3), 118.9–134.9 (m, phenyls) ppm. $^{31}P\{^{1}H\}$ (121.49 MHz, CD_2Cl_2): δ = 22.8 (s) ppm. Anal. Calcd for $C_{38}H_{36}Cl_4P_2Zn$ (761.84): C, 59.91; H, 4.76. Found: C, 60.20; H, 4.74.

$(Ph_3PMe)_2[ZnCl_3(DMF)]$: ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 2.94 (s, 3H, NCH_3, *coord.* DMF), 3.02 (s, 3H, NCH_3, *coord.* DMF), 3.03 (d, 3H, $^2J_{P–H}$ = 13.2 Hz, PCH_3), 7.67–7.92 (m, 15H, phenyls), 8.15 (s, 1H, O=CH) ppm. $^{13}C\{^1H\}$ (75.48 MHz, CD_2Cl_2): δ = 10.3 (d, $^1J_{P–C}$ = 57.9 Hz, PCH_3), 32.2 (s, NCH_3), 37.5 (s, NCH_3), 118.4–135.2 (m, phenyls), 165.3 (s, HC=O) ppm. $^{31}P\{^1H\}$ (121.49 MHz, CD_2Cl_2): δ = 22.5 (s) ppm. Anal. Calcd for $C_{22}H_{25}Cl_3NOPZn$ (522.16): C, 50.60; H, 4.83; N, 2.68. Found: C, 50.25; H, 4.91; N, 2.60.

$[Ph_2PMe_2](ZnCl_4)$: ^{1}H NMR (300.13 MHz, CD_3CN): δ = 2.58 (d, 12H, $^2J_{P–H}$ = 14.2 Hz, PCH_3), 7.67–7.92 (m, 20H, phenyls) ppm. $^{13}C\{^1H\}$ (75.48 MHz, CD_3CN): δ = 8.8 (d, $^1J_{P–C}$ = 57.0 Hz, PCH_3), 120.5–134.6 (m, phenyls) ppm. $^{31}P\{^1H\}$ (121.49 MHz, CD_3CN): δ = 22.1 (s) ppm. Anal. Calcd for $C_{28}H_{32}Cl_4P_2Zn$ (637.70): C, 52.74; H, 5.06. Found: C, 52.72; H, 4.84.

$[PhPMe_3]_2(ZnCl_4)$: ^{1}H NMR (300.13 MHz, CD_3OD): δ = 2.21 (d, 18H, $^2J_{P–H}$ = 14.6 Hz, PCH_3), 7.64–7.98 (m, 10H, phenyls) ppm. $^{13}C\{^1H\}$ (75.48 MHz, CD_3OD): δ = 8.27 (d, $^1J_{P–C}$ = 57.0 Hz, PCH_3), 129.6–134.1 (m, phenyls) ppm. $^{31}P\{^1H\}$ (121.49 MHz, CD_3OD): δ = 23.4 (s) ppm. Anal. Calcd for $C_{18}H_{28}Cl_4P_2Zn$ (513.56): C, 42.09; H, 5.49. Found: C, 41.83; H, 5.21.

In the case of $PMePh_2$, a zincated zwitterionic compound similar to **4** (*vide infra*) was detected by *in situ* NMR experiments. Its sensitivity towards hydrolysis prevented its isolation. *In situ* ^{1}H NMR (300.13 MHz, CD_2Cl_2): *δ* 1.25 (d, 4H, $^2J_{P–H}$ = 16.0 Hz, PCH_2-Zn), 2.40 (d, 6H, $^2J_{P–H}$ = 13.2 Hz, PCH_3), 7.48–7.84 (m, 20 H, phenyls). $^{13}C\{^1H\}$ (75.48 MHz, CD_2Cl_2): 0.6 (d, $^1J_{P–C}$ = 39.7 Hz, PCH_2), 12.0 (d, $^1J_{P–C}$ = 62.8 Hz, PCH_3), 126.9–133.0 (m, phenyls). $^{31}P\{^1H\}$ (121.49 MHz, CD_2Cl_2): *δ* 28.3 (s).

Reaction with P(*n*-Bu_3)

We achieved methylation of P(*n*-Bu_3) following the same procedure as described above for PPh_3 (using 0.23 g of P(*n*-$Bu)_3$, 0.28 mL, 1.14 mmol). The conversion, based on NMR, is 98%. Selected data of the phosphonium cation.

$[(n\text{-}Bu)_3PMe]_2(ZnCl_4)$: ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 0.87-0.97 (m, 9H, -$CH_2CH_2CH_2CH_3$),

1.35-1.60 (m, 12H, -$CH_2CH_2CH_2CH_3$), 1.90-2.03 (m, 6H, -$CH_2CH_2CH_2CH_3$), 2.24 (m, 3H, simulated, $^2J_{P–H}$ = 11.4 Hz, $^4J_{H-H}$ = 4.3 Hz, P-CH_3) ppm. $^{13}C\{^1H\}$ (75.48 MHz, CD_2Cl_2): δ = 8.8 (d, $^1J_{C–H}$ = 48 Hz). $^{31}P\{^1H\}$ (121.49 MHz, CD_2Cl_2): δ = 32.6 (s) ppm.

Using MeCN (10 mL) together with CH_2Cl_2 as solvent and without the hydrolysis step, a complex likely to be analogous to **4** was observed. Selected spectroscopic data: ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 0.55 (d, 3H, $^2J_{P–H}$ = 15.2 Hz; P-CH_3); $^{13}C\{^1H\}$ (75.48 MHz, CD_2Cl_2): δ = -3.5 (d, $^1J_{C–P}$ = 37.7 Hz; P-CH_3). $^{31}P\{^1H\}$ (121.49 MHz, CD_2Cl_2): δ = 37.9 (s) ppm.

Synthesis of 4.

PPh_3 (0.403 g, 1.54 mmol) was added to a suspension of anhydrous $CoCl_2$ (0.100 g, 0.77 mmol) in CH_2Cl_2 (20 mL) and MeCN (20 mL). The suspension was stirred for 20 min, giving rise to a deep blue solution to which Zn powder was added (0.325 g, 5.00 mmol). The colour of the reaction mixture turned green and was stirred until discoloration (12 h). The suspension was filtered *via* a cannula. Diethyl ether was layered onto the solution, giving colourless crystals of **4**, which were washed with Et_2O. Yield, based on PPh_3: 0.530 g, 85%. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 1.48 (d, 4H, $^2J_{P–H}$ = 15.8 Hz, PCH_2), 7.45–7.75 (m, 30H, phenyls) ppm. $^{13}C\{^1H\}$ (75.48 MHz, CD_2Cl_2): δ = 0.63 (d, $^1J_{P–C}$ = 39.6 Hz, PCH_2), 124.8–133.1 (m, phenyls) ppm; $^{31}P\{^1H\}$ (121.49 MHz, CD_2Cl_2): δ = 32.1 (s) ppm. Anal. Calcd for $C_{38}H_{34}Cl_4P_2Zn_2$ (825.21): C, 55.31; H, 4.15. Found: C, 55.18; H, 4.43.

Compound **4**·$ZnCl_2$ was prepared in a similar manner, without MeCN as a co-solvent, by layering pentane on the dichloromethane solution obtained after filtration. Its NMR spectra are similar to those of **4**. In the solid state, **4**·$ZnCl_2$ is much more sensitive towards hydrolysis then **4**, preventing to obtain satisfactory elemental analyses.

Reaction of $[CoCl(PPh_3)_3]$ with CH_2Cl_2, crystallization of 5·1/2C_6H_{14}.

Complex $[CoCl(PPh_3)_3]$ (0.300 g, 0.340 mmol) was dissolved in CH_2Cl_2 (50 mL). The green reaction mixture was stirred for 20 min, whereupon its colour turned blue progressively. Hexane was layered onto the solution, giving colourless crystals of PPh_3, deep blue crystals of $[CoCl_2(PPh_3)_2]$ and blue crystals of **5**·1/2C_6H_{14}. Its sensitivity towards hydrolysis prevented its isolation from the aforementioned species.

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