The reactivity of 1,1-dichloro-2,2-di-*tert*-butyldiphosphane towards lithiated metal carbonyls. The new entry to phosphanylphosphinidene dimers.

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Supporting information

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This pdf file includes:

1. Materials and methods
2. Experimental details and spectroscopic data.
3. Crystallographic details.
4. DFT calculation details.
5. References.

1. Materials and methods

THF was dried over K/benzophenone and distilled under argon. Pentane was dried over Na/benzophenone/diglyme and distilled under argon. All manipulations were performed in flame-dried Schlenk-type glassware on a vacuum line. Solution ^{31}P, ^{13}C, and ^{1}H spectra were recorded on Bruker AV300 MHz, Bruker AV400 MHz, BrukerAV600 MHz and Varian 500 MHz spectrometers (external standard TMS for ^{1}H, ^{13}C; 85% H_3PO_4 for ^{31}P) at ambient temperature. A literature methods were used to prepare $[Cp^*M(CO)_3]Li$ (M= Mo or W)[1] and *t*-$Bu_2P–PCl_2$.[2]

2. Experimental details and spectroscopic data

2.1 Reaction of $[Cp^*Mo(CO)_3]Li$ with *t*-Bu_2P-PCl_2 (mol ratio 1:1). Synthesis of $[Cp^*Mo(CO)_3\{\eta^2$-*t*-$Bu_2P–P(Cl)\}]$ **1-Mo**.

10 mL of solution of $[Cp^*Mo(CO)_3]Li$ (c= 0,1 M; 1 mmol) in THF was added dropwise to 10 mL of solution of *t*-Bu_2P-PCl_2 (c= 0,1 M, 1 mmol) in pentane at −70 °C. During the reaction, the color of the solution changed from dark brown to red. The solution was then warmed up to room temperature. The volume was reduced to one half under reduced pressure and the resulting solution was analyzed by $^{31}P\{^{1}H\}$, ^{31}P, and ^{1}H NMR. **1-Mo** was identified in solution. The solvent was then evaporated under reduced pressure and the residue extracted with 10 mL of pentane. The extract was filtrated, reduced to one half under reduced pressure. Then the solution was held at -30 °C and small amount of orange crystals of **2-Mo** deposited within few days. The examination of the $^{31}P\{^{1}H\}$-NMR of the reaction mixture indicates **1-Mo**, *t*-Bu_2PH, *t*-Bu_2PCl.

1-Mo: $^{31}P\{^{1}H\}$: δ 133.2 (d, $^{1}J_{PP}$ = 579 Hz, PCl); 63.8 (d, $^{1}J_{PP}$ = 579 Hz, *t*-Bu_2P);

2.2 Reaction of $[Cp^*Mo(CO)_3]Li$ with *t*-Bu_2P-PCl_2 (molar ratio 2:1). Synthesis of $[Cp^*Mo(CO)_2\{\eta^2$-*t*-$Bu_2P–P\}]_2$ (**2-Mo**).

20 mL of solution of $[Cp^*Mo(CO)_3]Li$ (c= 0,1 M; 2 mmol) in THF was added dropwise to 10 mL of solution of *t*-Bu_2P-PCl_2 (c= 0,1 M, 1 mmol) in pentane at −70 °C. During the reaction, the color of the solution changed from dark brown to red. The solution was then warmed up to room temperature. The volume was reduced to one half under reduced pressure and the resulting solution was analyzed by $^{31}P\{^{1}H\}$, ^{31}P, and ^{1}H NMR. The solvent was then evaporated under reduced pressure and the residue extracted with 10 mL of pentane. The extract was filtrated, reduced to one half under reduced pressure and stored at room temperature. The dark precipitate of **3-Mo** formed after few days. Then the solution filtered and was held at -30 °. Orange crystals of **2-Mo**· $0{,}5C_5H_{12}$ deposited within 24 h (190 mg, yield 41%). Elemental analysis: found %, C = 52.73, H = 7.28, calc. % for $C_{40}H_{66}Mo_2O_4P_4$,0.5(C_5H_{12}), C = 53.02, H = 7.54.

2-Mo: $^{31}P\{^{1}H\}$ (AA'XX' spin system): δ 79.8 (A, *t*-Bu_2P); -139.5 (X, P); $^{1}J_{AX}$ = 558, $^{2}J_{AX'}$ = 11 Hz, $^{3}J_{AA'}$ = 3 Hz, $^{1}J_{XX'}$ = 348 Hz, ^{1}H: δ 1.94 (s, 30H, (CH_3)$_5$C$_5$), 1.83 (d, $^{3}J_{PH}$ = 14.3 Hz, 18H, (CH_3)$_3$C), 1.04 (d, $^{3}J_{PH}$ = 14.5 Hz, 18H, (CH_3)$_3$C).

2.3 Reaction of [Cp*W(CO)$_3$]Li with *t*-Bu_2P-PCl_2 (molar ratio 1:1). Synthesis of [Cp*W(CO)$_3${η^2-*t*-Bu_2P–P(Cl)}] (**1-W**).

10 mL of solution of [Cp*W(CO)$_3$]Li (c= 0,1 M; 1 mmol) in THF was added dropwise to 10 mL of solution of *t*-Bu_2P-PCl_2 (c= 0,1 M, 1 mmol) in pentane at −70 °C. During the reaction, the color of the solution changed from dark brown to red. The solution was then warmed up to room temperature. The volume was reduced to one half under reduced pressure and the resulting solution was analyzed by $^{31}P\{^{1}H\}$, ^{31}P, and ^{1}H NMR. The complex **3** was identified in solution as transient specie. The solvent was then evaporated under reduced pressure and the residue extracted with 10 mL of pentane. The extract was filtrated, reduced to one half under reduced pressure. Then the solution was held at -30 °C and small amount of orange crystals of **2-W** deposited within few days. Results of the examination of the $^{31}P\{^{1}H\}$-NMR of the reaction mixture: **1-W**, *t*-Bu_2PH, *t*-Bu_2PCl.

1-W: $^{31}P\{^{1}H\}$: δ 151.8 (d, $^{1}J_{PP}$ = 447 Hz, PCl); 63.8 (d, $^{1}J_{PP}$ = 447 Hz, *t*-Bu_2P);

2.4 Reaction of [Cp*W(CO)$_3$]Li with *t*-Bu_2P-PCl_2 (molar ratio 2:1). Synthesis of [Cp*W(CO)$_3${η^2-*t*-Bu_2P–P}]$_2$ **2-W**.

20 mL of solution of [Cp*W(CO)$_3$]Li (c= 0,1 M; 2 mmol) in THF was added dropwise to 10 mL of solution of *t*-Bu_2P-PCl_2 (c= 0,1 M, 1 mmol) in pentane at −70 °C. During the reaction, the color of the solution changed from dark brown to red. The solution was then warmed up to room temperature. The volume was reduced to one half under reduced pressure and the resulting solution was analyzed by $^{31}P\{^{1}H\}$, ^{31}P, and ^{1}H NMR. The solvent was then evaporated under reduced pressure and the residue extracted with 10 mL of pentane. The extract was filtrated, reduced to one half under reduced pressure and stored at room temperature. The dark precipitate of **3-W** formed after few days. Then the solution was filtered and held at -30 °. Orange crystals of **2-W** deposited within 24 h (390 mg, yield 71%). Elemental analysis: found %, C = 42.81, H = 5.89, calc. % for $C_{40}H_{66}O_4P_4W_2$, C = 43.58, H = 6.03.

2-W: $^{31}P\{^{1}H\}$ (AA'XX' spin system): δ 47.8 (A, *t*-Bu_2P); -171.9 (X, P); $^{1}J_{AX}$ = 524, $^{2}J_{AX'}$ = 9 Hz, $^{3}J_{AA'}$ = 3 Hz, $^{1}J_{XX'}$ = 350 Hz; ^{1}H: δ 2.00 (s, 30H, (CH_3)$_5$C$_5$), 1.87 (d, $^{3}J_{PH}$ = 15.5 Hz, 18H, (CH_3)$_3$C), 1.07 (d, $^{3}J_{PH}$ = 14.7 Hz, 18H, (CH_3)$_3$C).

3. Crystallographic details

The diffraction data were collected with a KM4CCD kappa geometry diffractometer with graphite monochromated Mo Kα radiation (0.71073 Å) equipped with a Sapphire2 CCD detector (**2-W**) and a Sapphire3 CCD detector (**2-Mo**). The diffraction data for **3-Mo** was collected an STOE IPDS II diffractometer with graphite monochromated Mo Kα radiation (0.71073 Å). All measurements were carried out at low temperature (150K). Structures were solved by direct methods and refined against F^2 by least square techniques using the SHELXS and SHELXL software.[3] Refinement was performed with anisotropic temperature factors for all non-hydrogen atoms (disordered atoms were refined isotropically – **2-Mo**). Examination of the structure (**2-W**) with *PLATON*[4] showed that it contains large region between the molecules; these are occupied by pentane solvent molecule (0.5 molecule), but disorder is so extensive that an atomic model could not be developed. The solvent contribution was modeled by the *SQUEEZE* procedure of *PLATON*, from which an estimate of the solvent content was obtained on the basis of the volume of the voids and the approximate number of electrons in them. All hydrogen atoms were calculated on idealized positions.
CCDC numbers 1440633-1440635 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

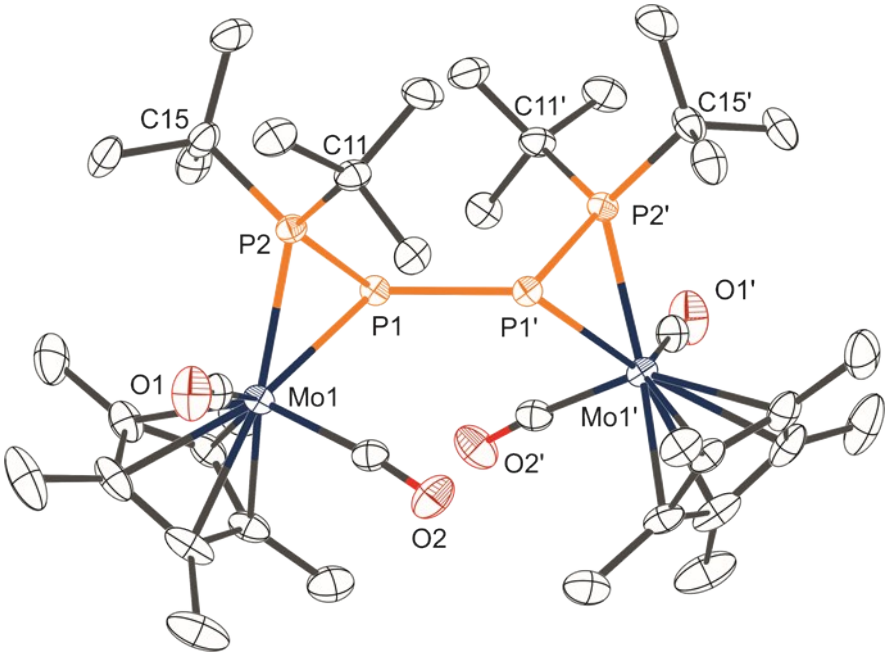

Figure S1 X-ray structure of the **2-Mo** showing the atom-numbering scheme. Ellipsoids drawn at the 50% probability level; H atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg.): Mo1-P1 2.5731(6), Mo1-P2 2.4450(6), P1-P2 2.1414(9), P1-P1 2.2413(12), Mo1-P1-P2 61.67(2), Mo1-P1-P1 108.04(4), P1-P1-P2 117.03(3), P1-P2-C15 119.94(8), P1-P2-C11 111.06(8), C11-P2-C15 109.95(11), ΣP1 = 286.74, ΣP2 = 340.94,

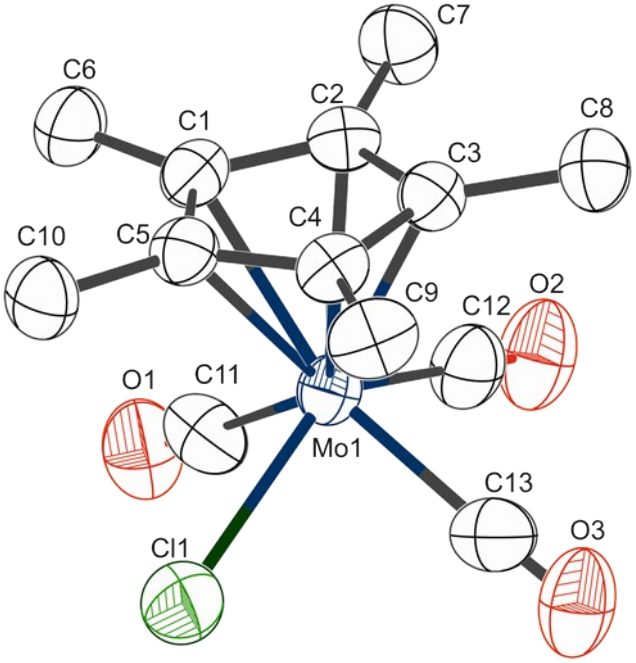

Figure S2 X-ray structure of the **3-Mo** showing the atom-numbering scheme. Ellipsoids drawn at the 50% probability level; H atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg.): Mo1-C1 2.368(4); Mo1-C2 2.316(4); Mo1-C3 2.299(4); Mo1-C4 2.325(4); Mo1-C5 2.382(4); Mo1-C11 2.068(6); Mo1-C12 2.025(6); Mo1-C13 2.073(7); Mo1-Cl1 2.5134(15); C1-Mo1-C11 89.37(19); C11-Mo1-C12 77.47(19); C11 Mo1 Cl1 79.71(14).

4. DFT calculation details

All calculations were performed using the Amsterdam Density Functional (ADF) package (version 2014.06).[3] DFT calculations were carried out using the hybrid-GGA functional B3LYP.[4] Relativistic effects were included with the scalar zero-order regular approximation (ZORA) model.[5] All atoms were described by a Slater-type triple-ζ quality basis set for all atoms with two polarization functions, corresponding to basis set TZ2P in the ADF package.[6] Starting geometries of **2-Mo** and [Cp*Mo(CO)$_3$(P(Cl)N*i*-Pr$_2$)][7] were taken from the experimental crystallographic data. Geometries for **1-Mo** and **4-Mo** were taken from corresponding parts of **2-Mo** and optimized using mentioned method.

Table S1 Calculated Hirshfeld charges for complexes **1-Mo**, **2-Mo, 4-Mo** and [Cp*Mo(CO)$_3$(P(Cl)N*i*-Pr$_2$)].[7]

Complex	Mo	P1	P2	N	Cl
[Cp*Mo(CO)$_3$(P(Cl)N*i*-Pr$_2$)]	0.325	0.159		-0.121	-0.163
1-Mo	0.282	0.015	0.171		-0.146
2-Mo	0.288	-0.025	0.186		
4-Mo	0.300	-0.121	0.166		

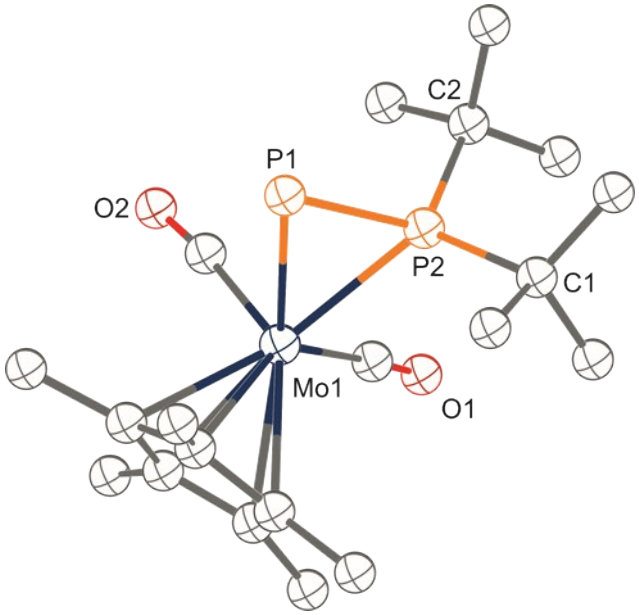

Figure S3 DFT optimized structure for **4-Mo**. Important bond lengths (Å) and bond angles (deg.): P1-P2 2.103; P1-Mo1 2.515; P2-Mo1 2.528: P2-C1 1.929; P2-C2 1.924; P2-P1-C1-P2-P1 114.26; C2-P2-P1 116.14; C1-P2-C2 110.64

Table S2 Cartesian coordinates of the optimized structure **1-Mo**.

C	-5.90900959	12.19885052	1.32764884
H	-6.64191853	11.52928801	1.78851084
H	-4.92664734	11.74566678	1.45479630
H	-6.12191621	12.23152423	0.26067731
C	-4.54334055	13.00992754	4.04798712
H	-3.98120422	13.54631919	4.80960328
H	-3.84283732	12.39646676	3.48221897
H	-5.22119319	12.32652233	4.57009056
C	-5.48994941	15.95440919	4.80903366
H	-6.13792827	15.58643091	5.61042348
H	-5.65342237	17.02660684	4.71838677
H	-4.45725512	15.80898808	5.12436056
C	-7.60021934	16.89457738	2.62350625
H	-7.94260518	17.21240374	1.64024149
H	-7.06574408	17.73211095	3.06916669
H	-8.48608583	16.70186385	3.23621794
C	-7.88946114	14.54674686	0.47222194

H	-7.54795918	13.92621480	-0.35541687
H	-8.11720064	15.53280324	0.07052660
H	-8.82533408	14.11655436	0.84206313
C	-4.26218793	14.51384204	-0.33639973
O	-4.05510783	13.92058020	-1.30630254
C	-5.98202909	13.55977261	1.95861411
C	-5.33316465	13.93858031	3.17292200
C	-5.79417512	15.23891292	3.52810747
C	-6.74101832	15.66501439	2.54046972
C	-6.87068741	14.61391237	1.57431863
C	-0.95709254	14.90540076	2.09319688
C	-1.41274848	14.84335844	3.55692418
H	-0.78553832	14.12370738	4.09066505
H	-2.44498865	14.51564095	3.64412866
H	-1.31777664	15.81013610	4.04949151
C	-0.98808531	13.48420434	1.50202468
H	-0.64476189	13.45279612	0.46931789
H	-1.99433377	13.06575166	1.53338225
H	-0.33293193	12.83498280	2.08985905
C	0.47709147	15.45438237	2.08110090
H	0.52561540	16.46377048	2.48874912
H	0.92825065	15.45532621	1.09213140
H	1.09596934	14.81315932	2.71632552
C	-1.44574482	16.73201269	-0.45338471
C	-0.75525773	15.62275036	-1.26893775
H	-1.44881895	14.82996807	-1.54837092
H	0.09224883	15.17789928	-0.75235766
H	-0.37381623	16.06632278	-2.19273113
C	-0.43526588	17.83389479	-0.08222933
H	0.40983433	17.46079716	0.48816335
H	-0.91043203	18.63454673	0.48135972
H	-0.04157092	18.26480814	-1.00727874

C	-2.53258586	17.36126129	-1.33792985
H	-2.03664449	17.79991509	-2.20842373
H	-3.07177741	18.15520208	-0.82933725
H	-3.24592238	16.62674091	-1.70294008
C	-5.37420985	16.88802893	0.10735122
O	-5.88830889	17.66076310	-0.57994882
P	-3.32249708	17.27840106	2.45449530
P	-2.25017997	15.96707777	1.12484067
Mo	-4.71045033	15.50606007	1.32738035
Cl	-3.38292382	19.28381777	1.64292476

Table S3 Cartesian coordinates of the optimized structure **4-Mo**.

C	-6.06255400	12.21713200	1.43075600
H	-6.75291700	11.58851900	2.00162400
H	-5.07879300	11.75248200	1.48238700
H	-6.38354800	12.19495200	0.39059400
C	-4.50762800	13.11260300	4.00573800
H	-3.89780100	13.65953500	4.72158000
H	-3.84548600	12.46935600	3.42603600
H	-5.16969500	12.45701000	4.58130100
C	-5.31469000	16.14477000	4.66203100
H	-6.01235600	15.94065300	5.48055200
H	-5.32470000	17.21737100	4.47731100
H	-4.31504100	15.88405500	5.00627200
C	-7.48526100	17.04899400	2.53469900
H	-7.84774700	17.34135900	1.55039300
H	-6.89579900	17.87695900	2.92673800
H	-8.35723300	16.92752000	3.18500600
C	-7.99313000	14.59944300	0.54403800
H	-7.73087200	13.91058900	-0.25806400
H	-8.19129300	15.56912300	0.09022700
H	-8.92840700	14.24709600	0.99019600

C	-4.16500000	14.23108700	-0.27983500
O	-3.89238500	13.48627700	-1.12042800
C	-6.05372900	13.61256200	1.98562100
C	-5.32012600	14.02979500	3.13865000
C	-5.70761500	15.36825000	3.44140600
C	-6.68670900	15.77856500	2.47934800
C	-6.91289400	14.67887000	1.58452000
C	-0.97746600	15.06901600	2.07527500
C	-1.46775800	15.18039200	3.52409900
H	-0.82977000	14.56263400	4.16281800
H	-2.49130200	14.83219200	3.62908100
H	-1.42390600	16.20840400	3.88341400
C	-0.95973800	13.58694800	1.66090800
H	-0.59717700	13.44302300	0.64401400
H	-1.95461800	13.14615500	1.72636600
H	-0.29821000	13.03001200	2.33121200
C	0.44578900	15.64560100	2.02339100
H	0.46585200	16.69718000	2.30986600
H	0.91455400	15.54054600	1.04766000
H	1.06707800	15.09786500	2.73902300
C	-1.44992000	16.56158900	-0.68037100
C	-0.72587400	15.39609200	-1.37662200
H	-1.39947600	14.56391400	-1.58054100
H	0.12175600	15.02235700	-0.80520100
H	-0.33696200	15.74857200	-2.33650100
C	-0.47707100	17.72850600	-0.42312500
H	0.38383600	17.44360100	0.17485100
H	-0.98293000	18.55617000	0.07467600
H	-0.10365400	18.09223600	-1.38497300
C	-2.54830900	17.07927200	-1.61948200
H	-2.06961800	17.45339800	-2.52885800
H	-3.10841100	17.90045600	-1.17528100

H	-3.24845000	16.29912200	-1.90946100
C	-5.42320300	16.65360000	-0.20106800
O	-5.95887000	17.33039300	-0.97121500
P	-3.41070300	17.47284900	1.92299000
P	-2.26099000	15.99225800	0.96933600
Mo	-4.72246100	15.45743700	1.18563200

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