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Conformationally Constrained N-Heterocyclic Phosphine−Diimine with Dual Functionality

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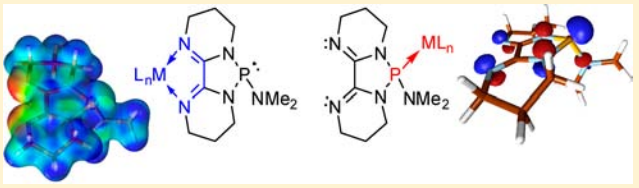
Supporting Information

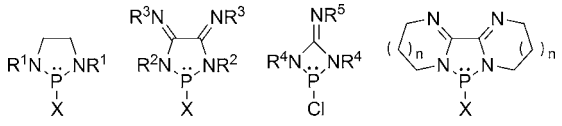
ABSTRACT: Condensation of octahydro-2,2′-bipyrimidine with $P(NMe_2)_3$ gave a 1,3,2-diazaphospholidine−4,5-diimine **4a** in which the "open" (exo/exo) conformation of the diimine unit was enforced by incorporation into a tricyclic molecular backbone. The coordination behavior of this potentially ambident ligand was sampled in reactions with ([(nbd)W-$(CO)_4$] and $[CpCo(CO)_2]$) and pnictogen halides ECl_3 (E = P, As, Sb). While PCl_3 reacted under ring metathesis, all other reactions gave isolable complexes of composition (**4a**)ML_n (ML_n = $W(CO)_5$, CpCo(CO), $AsCl_3$, $SbCl_3$); attempted recrystallization of the As-adduct yielded a complex (**4a**)$(AsCl_3)_2$ which was also accessible from reaction of **4a** with 2 equiv of $AsCl_3$. Single-crystal X-ray diffraction studies revealed that the ligand in [(**4a**)$W(CO)_5$] and [(**4a**)CpCo(CO)] binds through its phosphorus lone-pair; [(**4a**)$SbCl_3$] and [(**4a**)$(AsCl_3)_2$] contain a T-shaped ECl_3 unit which binds to the chelating diimine moiety, and associate further via chloride bridges to give centrosymmetric dimers. Reactions of **4a** with excess metal substrates gave no evidence that formation of bimetallic complexes with μ-bridging $1\kappa^2(N,N')$-$2\kappa P$-coordination is feasible; the extra $AsCl_3$ moiety in [(**4a**)$(AsCl_3)_2$] avoids this coordination mode by interacting with the peripheral chlorides of the central core. The observed selectivity suggests that ligand **4a** specifically addresses transition metal centers with low positive charge and some back-bonding capacity through the phosphorus lone-pair, and electrophiles that behave essentially as "pure" Lewis acids through the diimine unit. This assumption was confirmed by DFT studies which disclosed further that binding of the first metal center deactivates the opposite binding site and thus strongly inhibits the formation of dinuclear complexes.



INTRODUCTION

1,3,2-Diazaphospholidines **1**[1] (Chart 1) are known as versatile ligands which attract growing attention for various uses, in particular in catalysis. Specific derivatives have been applied in cross-coupling reactions,[2−4] and chiral diazaphospholidines were applied as useful ligands in enantioselective addition or substitution reactions[5,6] and in asymmetric hydroformylation.[7]

Chart 1. 1,3,2-Diazaphospholidines 1 (R^1 = alkyl, aryl; X = Ph, Cl, OR^1), 1,3,2-diazaphospholidine-4,5-diimines 2a (R^1 = 2,6-$iPr_2C_6H_3$, R^2 = Mes, X = Cl), 2b (R^1 = R^2 = 2,6-$Me_2C_6H_3$, X = Ph), 4 (X = any substituent), and 4-imino-1,3,2-diazaphosphetidines 3 (R^4, R^5 = Aryl)



The ligands used to date lack any functional modification of their heterocyclic rings, making thus the phosphorus atom the only metal binding site. We have recently introduced 1,3,2-diazaphospholidine-4,5-diimines **2**[8,9] which combine the *P*-donor function with two imine moieties that are part of an oxalamidine unit. Oxalamidines, like diimines in general,[10] form stable chelate complexes with various transition metals,[11−13] and the heterocycles **2** are thus potentially ditopic ligands which exhibit two metal binding sites with different characteristics. Considering that the rigid molecular skeleton orientates both donor sets into opposite directions in space, these species can be pictured as a special type of Janus-faced ligands[14−16] which attract interest due to their ability to accommodate two different metal atoms in close spatial proximity.[17] First studies on the coordination properties of the P−Cl and P−Ph substituted derivatives **2a,b** revealed, however, that these compounds show no dual functionality but bind to metals exclusively via the nitrogen donor atoms.[9] The diazaphospholidine−diimines differ in this respect from the cyclic guadinates **3**[18] which were recently reported by the group of Ragogna. These ring contracted monoimino analogs of **2** may bind Lewis acids via the exocyclic imine function, but the reported reaction with a Pt(0) substrate, which proceeded under ring fragmentation to give an iminophosphonium complex, indicates that also some P-activity may be retained.

A heuristic explanation for the one-sided coordination behavior of **2a,b** was found in the argument that the combined electron withdrawing effect of two imino-groups reduces the nucleophilicity at the phosphorus atom to an extent that metal

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Table 1. X-ray Details for 7, 8, 9, and 10·$AsCl_3$

	7	8	9	10·$AsCl_3$
empirical formula	$C_{15}H_{18}N_5O_5PW$	$C_{16}H_{23}CoN_5OP$	$C_{10}H_{18}Cl_3N_5PSb$	$C_{20}H_{38}As_4Cl_{12}N_{10}P_2{\times}2CH_2Cl_2$
formula weight (g mol^{-1})	563.16	391.29	467.36	1373.46
T (K)	123(2)	100(2)	100(2)	100(2)
crystal size (mm)	0.30 × 0.15 × 0.10	0.25 × 0.20 × 0.06	0.17 × 0.12 × 0.08	0.22 × 0.12 × 0.06
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
a (Å)	9.670(1)	10.7252(3)	23.3068(14)	9.9973
b (Å)	12.722(1)	9.7294(3)	9.4569(6)	19.5332(5)
c (Å)	31.666(3)	16.8025(5)	15.7720(10)	12.3096(3)
β (deg)	91.04(1)	95.431(2)	105.640(2)	93.339(2)
V ($Å^3$)	3895.0(6)	1745.47(9)	3347.6(4)	2399.7(1)
Z	8	4	8	2
D_c (Mg m^{-3})	1.921	1.489	1.855	1.901
μ (mm^{-1})	6.050	1.088	2.220	3.752
F(000)	2176	816	1840	1352
θ range (deg)	2.93−25.02	3.21−27.88	3.37−28.86	4.14−27.86
reflections collected	6671	19478	14652	47436
unique reflections	6671	4130	4128	5692
R_{int}	0.00[a]	0.06	0.03	0.13
max./min transmission	0.5818/0.3622	0.9182/0.6967	0.8424/0.7041	0.7736/0.5058
data/restraints/parameters	6671/60/493	4130/0/217	4128/0/183	5692/0/246
G.o.F. on F^2	1.024	1.063	1.025	1.134
$R1$ [$I > 2\sigma(I)$]	0.0689	0.0338	0.0259	0.0486
$wR2$ (F^2)	0.1852	0.0857	0.0538	0.1033
largest diff. peak and hole (e $Å^{-3}$)	1.878 and −2.869	0.040 and −0.453	0.686 and −0.453	0.678 and −0.840

[a]Nonmerohedral twin with three domains.

coordination at this site is disfavored.[9] Furthermore, the predisposition of **2a,b** to bind as chelating diimine is also far from perfect, as this requires an energetically unfavorable[9] isomerization from the native endo/exo- to an "open" exo/exo-conformation which diminishes both the thermodynamic stability and kinetic accessibility of the complexes. In principle, it should be feasible to overcome these intrinsic deficiencies by appropriate tuning of the molecular structure. Considering that tris(alkylamino) phosphines are strongly electron donating ligands,[19−21] attachment of a P-dialkylamino substituent is expected to improve the P-nucleophilicity of a diazaphospholidine-4,5-diimine, and incorporating the diimine unit into a suitable polycyclic ring system should allow to lock the CN double bonds in the "open" conformation and thus solve the conformational problem.

Starting from these hypotheses, we identified tricyclic diazaphospholidine-diimines **4**, **5** as promising target compounds for further studies. In this contribution, we report on the synthesis of a derivative **4a** (with X = NMe_2) starting from an octahydro-dipyrimidine precursor, and on first coordination chemical studies which allow to verify the expected behavior as ambident ligand with dual functionality.

EXPERIMENTAL SECTION

All manipulations were carried out under an atmosphere of dry argon using standard vacuum line techniques. Solvents were dried by standard procedures. 2,2′-Octahydrobipyrimidine **6** was prepared as previously described.[22] All other chemicals were commercially available and used as received. Solution NMR spectra were recorded on a Bruker Avance 250 (^{1}H, 250.1 MHz; ^{13}C, 62.8 MHz; ^{31}P, 101.2 MHz) spectrometer at 303 K. Solid-state NMR spectra were recorded with a Bruker Avance 400 spectrometer (^{31}P 161.9 MHz; ^{13}C 100.5 MHz, ^{15}N 40.4 MHz) equipped with a 4 mm MAS probe. MAS experiments were performed using standard ZrO_2 rotors and spinning speeds between 8 and 9 kHz for ^{13}C and ^{15}N NMR spectra and 14 kHz for ^{31}P NMR spectra. Cross-polarization was applied using a ramp-shaped contact pulse and mixing times between 0.8 and 5 ms unless noted. Chemical shifts are referenced to external $SiMe_4$ (^{1}H, ^{13}C), ext. 85% H_3PO_4 (Ξ = 40.480747, ^{31}P), or ext. neat $MeNO_2$ (Ξ = 10.136767 MHz, ^{15}N). Elemental analyses (C, H, N) were determined on a Perkin-Elmer 2400 CHN/O Analyzer; chlorine contents were determined by argentometric titration. Melting points were determined in sealed capillaries on a Büchi Melting Point B-545 apparatus. IR spectra were recorded on a Nicolet 6700 FTIR-spectrometer equipped with a Smart orbit ATR unit with a diamond crystal and a MCTA-detector. (+)-ESI mass spectra were recorded in methanolic solution on a Bruker Daltonics MicroTOF Q instrument.

Single crystal X-ray diffraction data were collected on a Bruker-Nonius Kappa CCD diffractometer at 123(2) or at 100(2) K using Mo Kα radiation (λ = 0.71073). Crystals were selected under Paratone-N oil, mounted on nylon loops, and immediately placed in a cold stream of N_2. Direct methods (SHELX-97[23]) were used for structure solution. Non-hydrogen atoms were refined anisotropically (SHELX-97, full-matrix, least-squares on F^2). Semiempirical absorption corrections from equivalents were applied. **7** is a nonmerohedral twin with three domains. Hydrogen atoms were refined using a riding model. Details of the crystal structure determinations are listed in Table 1. CCDC-922220 for **7**, CCDC-921453 for **8**, CCDC-921445 for **9**, and CCDC-921452 for **10·$AsCl_3$** 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.

Computational studies were performed with the Gaussian09[24] suite of programs using cc-pVDZ or cc-pVTZ basis sets for the light atoms up to As and cc-pVDZ-PP or cc-pVTZ-PP basis sets[25] (obtained from the Basis set exchange home page[26,27]) with electrostatic potentials (ECP) on the inner shells for W. Molecular structures were first energy optimized at the B3lyp/cc-pVDZ(-PP) level, and energies of the resulting minimum structures were then recalculated at the B3lyp/cc-pVTZ(-PP) level. Population analyses are based on the densities obtained at this level. The NBO analysis[28] was performed with the NBO 3.1 program as implemented in the Gaussian package.

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MOLDEN[29] was used for the visualization of Kohn−Sham orbitals and the electrostatic potential.

9-Dimethylamino-4,4′,8a,8a′-tetraaza-9-phospha-2,3,6,7,8,8a,9,9a-octahydro-1*H*-fluorene (4a). $P(NMe_2)_3$ (1.18 g, 7.2 mmol) was added to a solution of **6** (1.00 g, 6.0 mmol) in acetonitrile (30 mL). The mixture was refluxed for 3 h under a slow stream of argon to help removing the gaseous dimethylamine formed. After the gas evolution had ceased, the mixture was allowed to cool to room temperature, and volatiles were evaporated in vacuum. The product remained as a yellow oil (yield 680 mg, 94%) which did not solidify upon prolonged storage at 4 °C and was characterized by analytical and spectral data. The crude product was used in subsequent reactions without further purification. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 93.0 (s). ^1H NMR ($CDCl_3$): δ = 1.60 (m, 2 H, 5/5′-CH_2), 1.64 (m, 2 H, 5/5′-CH_2), 2.38 (d, $^3J_{PH}$ = 8.4 Hz, 6 H, NCH_3), 3.00 (m, 2 H, 6/6′-CH_2), 3.18 (m, 2 H, 6/6′-CH_2), 3.28−3.42 (m, 4 H, 4/4′-CH_2). ^{13}C NMR ($CDCl_3$): δ = 20.4 (d, $^3J_{PC}$ = 4.7 Hz, C-5/5′), 35.0 (broad d, $^2J_{PC}$ = 20 Hz, NCH_3), 39.2 (d, $^2J_{PC}$ = 17.7 Hz, C-6/6′), 43.9 (d, $^4J_{PC}$ = 1.1 Hz, C-4/4′), 148.6 (d, $^2J_{PC}$ = 5.5 Hz, C-2,2′). (+)-ESI-MS: 240.14 $[M + H]^+$, 167.13 $[MH^+ - PNMe_2]$. IR (cm^{-1}): $\tilde{\nu}$ = 1643 (s, C═N). Anal calcd for $C_{10}H_{18}N_5P$ (239.26): C 50.20, H 7.58, N 29.27. Found: C 49.70, H 7.71, N 28.95.

9-Dimethylamino-4,4′,8a,8a′-tetraaza-9-phospha-2,3,6,7,8,8a,9,9a-octahydro-1*H*-fluorene-tungstenpentacarbonyl (7). A solution of [(norbornadiene)$W(CO)_4$] (1.62 g, 4.2 mmol) in toluene (20 mL) was added to a solution of **4a** (1.00 g, 4.2 mmol) in toluene (25 mL). The resulting yellow solution was refluxed overnight. The reaction mixture, whose color had turned to a dark orange, was allowed to cool to room temperature and filtered over Celite. Evaporation of the solvent produced a bright orange powder which was recrystallized from toluene to give 1.80 g (76%) of **7**, mp. 156 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 103.9 (s, $^1J_{PW}$ = 333 Hz). ^1H NMR ($CDCl_3$): δ = 1.21 (m, 2 H, CH_2), 1.39 (m, 2 H, CH_2), 2.07 (d, $^3J_{PH}$ = 10.6 Hz, 6 H, NCH_3), 2.55 (m, 2 H, CH_2), 3.10 (m, 2 H, CH_2), 3.38 (m, 2 H, CH_2) 3.40 (m, 2 H, CH_2). ^{13}C NMR ($CDCl_3$) δ = 19.9 (d, $^3J_{PC}$ = 5.0 Hz, C-5/5′), 36.2 (d, $^2J_{PC}$ = 7.6 Hz, NCH_3), 38.6 (d, $^2J_{PC}$ = 8.4 Hz, C-6/6′), 44.2 (d, $^4J_{PC}$ = 0.7 Hz, C-4/4′), 144.9 (d, $^2J_{PC}$ = 1.41 Hz, C-2,2′), 195.5 (d, $^2J_{PC}$ = 9.0 Hz, $^1J_{WC}$ = 125.0 Hz, *cis*-CO), 197.4 (d, $^2J_{PC}$ = 31.1 Hz, *trans*-CO). (+)-ESI-MS: 564.07 $[M + H]^+$, 240.13 $[MH^+ - W(CO)_5]$. IR (cm^{-1}): $\tilde{\nu}$ = 2074 (s, νCO), 1909 (sh, νCO), 1895 (s, νCO), 1657 (s, νC═N). Anal calcd for $C_{15}H_{18}N_5O_5PW$ (563.15): C 31.99, H 3.22, N 12.44. Found: C 31.83, H 3.37, N 12.41.

9-Dimethylamino-4,4′,8a,8a′-tetraaza-9-phospha-2,3,6,7,8,8a,9,9a-octahydro-1*H*-fluorene-cyclopentadienylcobalt carbonyl (8). $CpCo(CO)_2$ (903 mg, 5.0 mmol) was added via syringe to a solution of **4a** (1.00 g, 4.2 mmol) in toluene (50 mL). The resulting solution was refluxed for 16 h at a bath temperature of 130 °C. The mixture, which had meanwhile turned dark red, was then allowed to cool to room temperature, and evaporated to dryness. The blackish residue was suspended in toluene (50 mL), and filtered over Celite. The filtrate was concentrated under reduced pressure to approximately half the original volume and stored at 4 °C. A small amount of a crystalline precipitate formed which was collected by filtration (no yield determined) and characterized by ^{31}P NMR and IR spectroscopy, analytical data, and a single-crystal X-ray diffraction study. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 145.2 (broad s). IR (cm^{-1}): $\tilde{\nu}$ = 1939 (s, νCO). Anal calcd for $C_{16}H_{23}CoN_5OP$ (406.33): C 50.25, H 6.45, N 17.24. Found: C 50.14, H 6.08, N 16.54.

9-Dimethylamino-4,4′,8a,8a′-tetraaza-9-phospha-2,3,6,7,8,8a,9,9a-octahydro-1H-fluorene-trichlorostibine complex (9). A solution of $SbCl_3$ (959 mg, 4.2 mmol) in THF (10 mL) was added dropwise to a solution of **4a** (1.00 g, 4.2 mmol) in THF (10 mL). After some minutes, a solid, greyish precipitate began to form. The mixture was stirred overnight and filtered. The solid residue was washed with THF and dried in vacuum to give 1.08 g of **9** (yield 2.3 mmol, 55%) as a fine, grayish powder, mp 92 °C. The filtrate was concentrated to half of its original volume and stored at −20 °C to give a further crop of crystalline product which was suitable for a single-crystal X-ray diffraction study. Due to its low solubility in common organic solvents, complex **9** was characterized by analytical data, IR, and CP/MAS NMR spectroscopy. $^{31}P\{^1H\}$ CP/MAS NMR: δ = 106.9. $^{13}C\{^1H\}$ CP/MAS NMR: δ = 18.5 (s, CH_2), 19.5 (s, CH_2), 30.9 (s, NCH_3), 37.2 (s, NCH_3), 37.6 (s, 2 NCH_2), 41.0 (s, NCH_2), 41.7 (s, NCH_2), 150.5 (s, C═N), 151.6 (s, C═N). $^{15}N\{^1H\}$ CP/MAS NMR: δ = −187.9 (s, C═N), −219.8 (broad s, C═N), −249.5 (d, $^1J_{PN}$ = 66 Hz, PN), −267.4 (d, $^1J_{PN}$ = 57 Hz, PN), −329.7 (d, $^1J_{PN}$ = 75 Hz, NMe_2). IR (cm^{-1}): $\tilde{\nu}$ = 1668 (m, νC═N), 1650 (s, νC═N). Anal calcd for $C_{10}H_{18}N_5Cl_3PSb$ (467.38): C 25.70, H 3.88, N 14.98, Cl 22.76. Found: C 25.26, H 3.65, N 14.65, Cl 22.98.

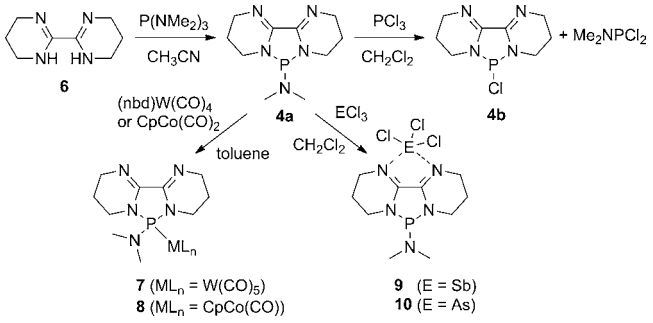
9-Dimethylamino-4,4′,8a,8a′-tetraaza-9-phospha-2,3,6,7,8,8a,9,9a-octahydro-1*H*-fluorene-trichloroarsine complex (10). A solution of $AsCl_3$ (762 mg, 4.2 mmol) in THF (10 mL) was added dropwise to a solution of **4a** (1.00 g, 4.2 mmol) in THF (10 mL). The color of the solution changed immediately from yellow to beige, and after some minutes, a solid precipitate began to form. The mixture was stirred overnight and filtered. The solid residue was washed with THF and dried in vacuum go give 1.30 g of **10** (3.34 mmol, yield 72%) as a beige colored, fine powder of mp 95 °C. Due to its low solubility in all common organic solvents, the product was characterized by analytical data and CP/MAS NMR spectroscopy. $^{31}P\{^1H\}$ CP/MAS NMR: δ = 114.6. $^{13}C\{^1H\}$ CP/MAS NMR: δ = 19.8 (s, 2 CH_2), 32.3 (s, NCH_3), 38.3 (s, 2 NCH_2), 38.6 (s, NCH_3), 41.6 (s, NCH_2), 42.3 (s, NCH_2), 149.2 (s, C═N), 151.8 (s, C═N). $^{15}N\{^1H\}$ CP/MAS NMR: δ = −175.5, −217.0, −244.3, −270.4, −326.6 (NMe_2). IR (cm^{-1}): $\tilde{\nu}$ = 1683 (m, νC═N), 1655 (m, νC═N). Anal calcd for $C_{10}H_{18}N_5Cl_3PAs$ (420.54): C 28.56, H 4.31, N 16.65, Cl 25.29. Found: C 28.68, H 4.33, N 16.52, Cl 25.05.

In order to grow single crystals, a sample of the product was suspended in hot CH_2Cl_2. The suspension was filtered, the filtrate concentrated to two-thirds of its original volume and stored at −20 °C. A crystalline solid formed which was collected by filtration and identified by analytical and solid-state NMR data and a single-crystal X-ray diffraction study as adduct **10**·$AsCl_3$. $^{31}P\{^1H\}$ CP/MAS NMR: δ = 121.3. $^{13}C\{^1H\}$ CP/MAS NMR: δ = 20.1 (s, CH_2), 21.0 (s, CH_2), 30.6 (s, NCH_3), 38.4 (s, NCH_2), 39.9 (s, NCH_2), 40.4 (s, NCH_3), 42.1 (s, NCH_2), 42.8 (s, NCH_2), 56.1 (s, CH_2Cl_2), 151.1 (s, C═N), 151.7 (s, C═N). Anal calcd for $C_{10}H_{18}N_5Cl_6PAs_2 \cdot CH_2Cl_2$ (686.75): C 19.24, H 2.94, N 10.20. Found: C 19.06, H 2.95, N 9.92.

RESULTS AND DISCUSSION

By analogy to the synthesis of **2**,[8,9] tricyclic target compounds **4**, **5** should in principle be accessible starting from appropriate cyclic oxalamidines like octahydro-bipyrimidine (**6**;[22] see Scheme 1) or 2,2′-bi-imidazoline, respectively. Anticipating that a ring system of three anellated five-membered rings exhibits substantial geometrical constraints which might limit the metal coordination ability of the diimine unit, we chose conformationally more flexible **6** for our further studies. Condensation with $P(NMe_2)_3$ in refluxing acetonitrile produced, after removal of all volatiles, an air and moisture

Scheme 1[a]



[a]nbd = norbornadiene, Cp = C_5H_5.

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sensitive, yellow oil which resisted all attempts to further purification by crystallization, distillation, or chromatography. The identity of the crude product as the targeted N-heterocyclic phosphine **4a** (Scheme 1) was nonetheless unambiguously established from analytical and spectral data.

The ^{31}P NMR chemical shift of 93.0 ppm is similar as in 2-dimethylamino-1,3-diphenyl-1,3,2-diazaphospholidine (97.6 ppm[30,31]) and lies at the high end of the known chemical shift range of 2-amino-1,3,2-diazaphospholenes (77.4 to 92.6 ppm[32]). The number of observable ^{1}H and ^{13}C NMR signals is in accord with the presence of a C_s-symmetrical molecule with two equivalent six-membered rings. The two NCH_2 units in each six-membered ring are anisochronic (which is not the case in **6** as a consequence of rapid 1,3-H-shifts), and at least two of three methylene units contains diastereotopic protons; both findings can be related to the presence of a configurationally stable (at least on the NMR time scale) pyramidal phosphorus atom in the central ring. The observation of a broadened ^{13}C NMR signal for the carbon atoms in the NMe_2-group indicates hindered rotation of this group around the PN single bond, which is not uncommon for aminophosphines.

In order to probe the coordination properties of **4a** toward transition metals, we chose to study exemplary reactions with $[(nbd)W(CO)_4]$ (nbd = norbornadiene) and $[CpCo(CO)_2]$, respectively. The labile diolefin or carbonyl ligands in these substrates are easily displaced by other Lewis bases, giving rise to complexes which may contain a plethora of P-donor ligands but also diimines[11−13,33−35] (a specific example is the reaction of $[(nbd)W(CO)_4]$ with **2b** to give the appropriate diimine complex[9]). As a consequence of such ambivalent behavior, these substrates seemed ideal candidates to monitor a possible competition between the two donor sites of **4a**.

Reaction of the ligand with both metal complexes in refluxing toluene yielded deeply colored solutions. ^{31}P NMR spectra of the reaction mixtures displayed, beside weak signals of unreacted starting material and unspecific decomposition products, a single resonance attributable to a metal complex, thus indicating that specific binding of the metal atoms to one of the two donor sites had occurred. Both complexes were isolated after appropriate workup and identified by analytical and spectroscopic measurements as well as single-crystal X-ray diffraction studies.

Key to the structural assignment of the reaction product of **4a** and $[(nbd)W(CO)_4]$ was the ^{31}P NMR spectrum, which displays a singlet at 103.9 ppm accompanied by a set of ^{183}W satellites with a large splitting of 333 Hz. Even if the small coordination shift ($\Delta\delta^{31}P^{coord} = \delta^{31}P(complex) - \delta^{31}P(ligand)$) of +10 ppm is of little diagnostic value, the magnitude of the coupling is typical for tungsten-phosphine complexes (cf. $^{1}J_{PW}$ = 310 Hz for $[(Me_2N)_3P]W(CO)_5$[36]) and implies that the metal binds through the phosphorus lone-pair and not the diimine unit. This assignment is backed by the finding that the νC═N vibrational mode of the free ligand **4a** experiences a slight blue shift upon formation of the tungsten complex, which is in marked contrast to the pronounced red shift induced by metal coordination at the diimine unit of the N-aryl diazaphospholidine−diimines **2a**,**b**.[9] The IR spectrum of the reaction product reveals further the distinctive three-band pattern of νCO vibrational modes that is commonly associated with a $W(CO)_5$ moiety and is also in accord with the presence of appropriate ^{13}C NMR signals attributable to CO ligands in *cis*- and *trans*-position to a metal bound phosphorus atom. Considering that the number and multiplicity of ^{1}H and remaining ^{13}C NMR signals confirms that the ligand has retained its structural integrity, we assigned the product the molecular structure of a phosphine complex **7** (Scheme 1). The hypotheses derived from the spectral data were readily confirmed by the results of a single-crystal X-ray diffraction study (Figure 1).

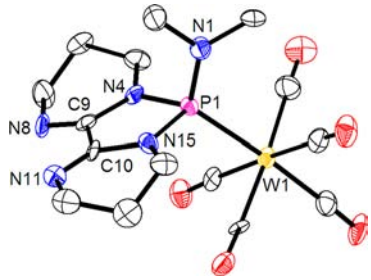

Figure 1. Molecular structure of **7**. Only one of two crystallographically independent molecules is shown; thermal ellipsoids are drawn at 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°, values for the second molecule in brackets): W(1)−P(1) 2.473(4) [2.493(4)], P(1)−N(1) 1.637(15) [1.653(15)], P(1)−N(15) 1.695(15) [1.703(15)], P(1)−N(4) 1.724(16) [1.697(15)], N(4)−C(9) 1.39(2) [1.40(2)], C(9)−C(10) 1.50(3) [1.48(3)], C(10)−N(15) 1.41(2) [1.36(2)], N(8)−C(9) 1.27(2) [1.30(2)], C(10)−N(11) 1.24(2) [1.28(2)], N(1)−P(1)−N(15) 104.7(8) [106.4(7)], N(1)−P(1)−N(4) 106.8(8) [106.8(8)], N(15)−P(1)−N(4) 89.8(8) [89.4(8)].

The crystal contains two crystallographically independent molecules which show no significant structural deviations. The octahedral and distorted tetrahedral coordination geometries around the tungsten and phosphorus atoms, respectively, are as expected. The central diazaphospholidine ring in the ligand is planar. The six-membered rings feature envelope conformations in which the central CH_2-groups in the trimethylene unit groups are bent out of the plane formed by the remaining ring atoms; the two envelope "flaps" adopt a transoid arrangement with respect to the central part of the ring system. The structural features of the diazaphospholidine-diimine moiety are (apart from the different imine stereochemistry) similar as in complexes of **2a**,**b**;[9] individual bond distances and angles display no peculiarities. The N(1) atom of the dimethylamino substituent displays a trigonal planar coordination environment; the C_2N plane is nearly parallel to the P−W bond and thus bisects the central heterocyclic ring. The exocyclic P(1)−N(1) distances are by some 5 pm shorter than the endocyclic ones; similar inequalities are also observed in other triaminophosphines and their complexes[19] and are believed to be intimately connected with the strong electron donor capabilities of these ligands.

The cobalt complex of **4a** gives rise to a ^{31}P NMR signal which is distinguished by a significant positive coordination shift ($\delta^{31}P$ = 145.2; $\Delta\delta^{31}P^{coord}$ = 51.9) and an amazingly large line width ($\Delta\nu_{1/2}$ = 300 Hz). This line broadening is typically a consequence of unresolved scalar coupling of the ^{31}P nucleus with a ^{59}Co (I = 9/2) spin, and suggests then that the metal atom binds, as in **7**, through the phosphorus atom. Even if further spectroscopic characterization of the product was impeded by its liability to dissociate in solution to give an unknown metal-containing product and free **4a**, a single-crystal X-ray diffraction study allowed to confirm this hypothesis and

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establish the molecular structure as carbonyl complex **8** (Scheme 1). The cobalt atom displays a pseudotrigonal coordination by a Cp anion, a CO, and neutral **4a** (Figure 2). The structural features of the tricyclic phosphine ligand are unpeculiar and match those in **7**.

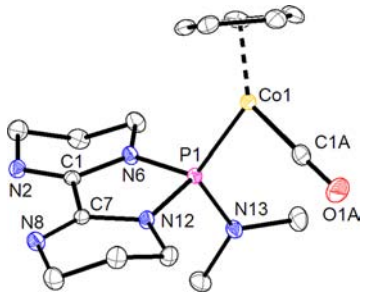

Figure 2. Molecular structure of **8**. Thermal ellipsoids are drawn at 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)−N(13) 1.6516(16), P(1)−N(6) 1.7068(16), P(1)−N(12) 1.7101(16), P(1)−Co(1) 2.1002(5), C(1)−N(2) 1.280(2), C(1)−N(6) 1.377(2), C(1)−C(7) 1.499(2), C(7)−N(8) 1.272(2), C(7)−N(12) 1.388(2), Co(1)−C(1A) 1.713(2), Co(1)−Z(Cp) 1.709(1), N(13)−P(1)−N(6) 106.09(8), N(13)−P(1)−N(12) 104.20(8), N(6)−P(1)−N(12) 88.88(7).

The formation of the metal pentacarbonyl complex **7** is readily explained by the assumption that the $W(CO)_4$-fragment of the starting material undergoes ligand redistribution in the course of the reaction to yield appropriate amounts of $W(CO)_5$ and a metal containing precipitate which was separated by filtration. As in the case of the previously reported complexes of **2a**,**b**,[9] we observed no evidence for the formation of dinuclear complexes with μ-bridging coordination of **4a**, even in the presence of an excess of metal complex. The observed switch from N,N-coordination of transition metal carbonyl fragments in the monocyclic ligands **2a**,**b** to P-coordination in **4a** suggests at first glance that the approach of introducing a P-NMe_2 group in order to enhance the P-basicity of the diazaphospholene−-4,5-diimine framework and stimulate metal coordination at this site proved fruitful. However, it cannot be excluded that other factors like better steric accessibility of the P-donor site in **4a** may play a role. Furthermore, since the metal−ligand bonding is affected by a balance of L → M σ-dative and M → L π-retrodative contributions, any observed reactivity must be considered to depend on the properties of both ligand and metal. In order to obtain a more comprehensive view, we wanted therefore to complement the studies on reactions of **4a** with low valent, ambiphilic W(0) and Co(I) centers by investigations on reactions with pure Lewis acidic substrates such as the pnictogen chlorides ECl_3 (E = P, As, Sb), which bind predominantly via the L → M σ-bonding contribution.

The reaction with PCl_3 produced according to a ^{31}P NMR spectroscopic assay a mixture of two phosphorus-containing products neither of which could be separated or isolated in pure form. One product was readily identified as the known Me_2NPCl_2 ($\delta^{31}P$ = 164) whereas the second species displays a similar ^{31}P chemical shift ($\delta^{31}P$ = 130) as **2a** ($\delta^{31}P$ = 134.6[8]) and was on this basis formulated as P-chloro phosphine **4b** (Scheme 1). Formation of both products is consistently explained as resulting from a similar ring metathesis reaction as had previously been observed in the reaction of **2b** with PBr_3. The reactions of **4a** with the heavier pnictogen halides produced colorless or off white, insoluble precipitates having elemental compositions that are consistent with a formulation of 1:1 adducts. Multinuclear (^{31}P, ^{13}C, ^{15}N) CP/MAS NMR measurements indicated that both solids contain a single phosphorus-containing species in which the molecular framework of the ligand **4a** is still intact. Whereas the ^{31}P NMR chemical shifts were of little diagnostic value and did not help in the identification of the coordination site, the ^{15}N NMR signals of the imino nitrogen atoms ($\delta^{15}N$ −175 to −220) appear more shielded than in amidines ($\delta^{15}N$ −135 to −170[37]) and gave a first indication that the ligand might interact with the Lewis acid via the diimine unit. This hypothesis was backed by the observation that the νC═N vibrational mode displays a splitting into two components that is absent in both the free ligand **4a** and the P-donor complexes **7**, **8** and finally confirmed by the result of a single-crystal X-ray diffraction study of the Sb-adduct which revealed the presence of a diimine complex **9** (Scheme 1; the molecular structure is shown in Figure 3). Attempts to grow suitable single-crystals for a crystallographic study of the As-adduct led to a surprising result: dissolution of the solid in hot CH_2Cl_2 was in this case accompanied by partial dissociation of the original product to give free ligand **4a** and a crystalline material that was readily identified as adduct of the diimine-$AsCl_3$ complex **10** with a further molecule of $AsCl_3$ (Figure 4). The same product was also accessible from direct reaction of **4a** with 2 equiv of $AsCl_3$.

Regardless of the different overall composition of **9** and **10**·$AsCl_3$, the basic building block is in both cases a molecular complex formed by interaction of the diimine unit of a ligand **4a** with the metal atom of a T-shaped ECl_3 unit. One of the E−N bonds formed (**9** Sb1−N2 2.171 Å; **10**·$AsCl_3$ As1−N8 1.982

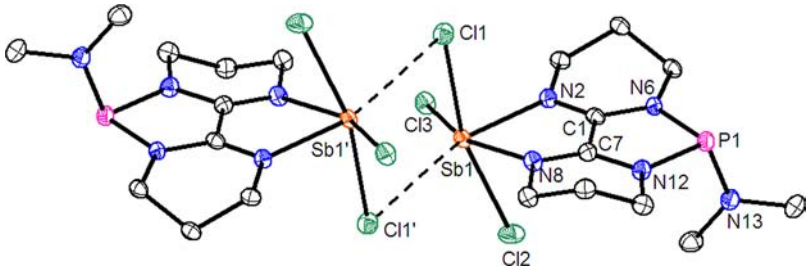

Figure 3. Molecular structure of **9**. Thermal ellipsoids are drawn at 50% probability level; hydrogen atoms are omitted for clarity, and symmetry dependent atoms were generated with the operator 0.5 − x, 0.5 − y, 1 − z. Selected bond distances (Å) and angles (deg): Sb(1)−N(2) 2.171(2), Sb(1)−N(8) 2.375(2), Sb(1)−Cl(1) 2.578(1), Sb(1)−Cl(2) 2.590(1), Sb(1)−Cl(3) 2.537(1), Sb(1)-Cl(1′) 3.590(1), C(1)−N(2) 1.298(3), C(1)−N(6) 1.328(3), C(1)−C(7) 1.469(3), C(7)−N(8) 1.287(3), C(7)−N(12) 1.340(3), N(6)−P(1) 1.774(2), N(12)−P(1) 1.753(2), P(1)−N(13) 1.639(2), Cl(1)−Sb(1)−Cl(2) 164.47(2).

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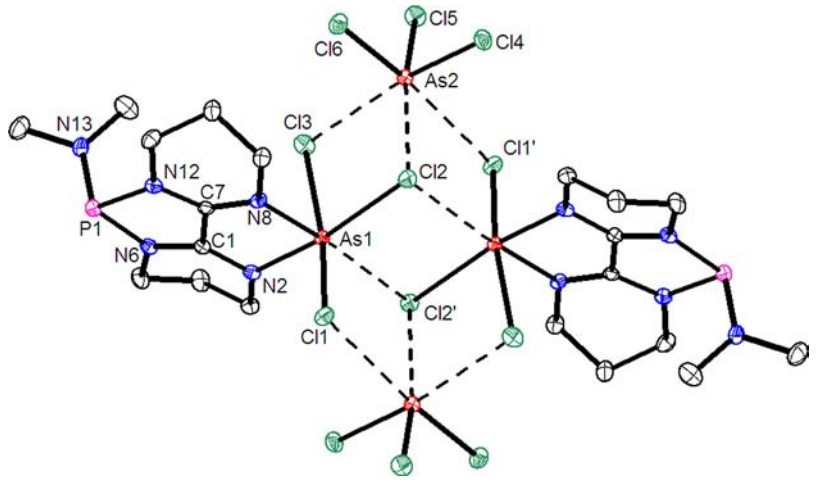
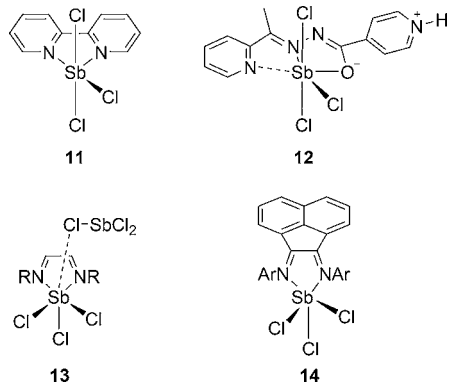


Figure 4. Molecular structure of **10·AsCl$_3$**. Thermal ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity, and symmetry dependent atoms were generated with the operator $2 - x$, $1 - y$, $1 - z$. Selected bond distances (Å) and angles (deg): As(1)−N(8) 1.982(4), As(1)−N(2) 2.012(4), As(1)−Cl(1) 2.323(1), As(1)−Cl(2) 2.779(1), As(1)−Cl(3) 2.713(1), As(1)-Cl(2′) 3.055(1), C(1)−N(2) 1.308(7), C(1)−N(6) 1.320(7), C(1)−C(7) 1.454(7), C(7)−N(8) 1.303(7), C(7)−N(12) 1.313(7), N(8)−C(9) 1.474(7), C(9)−C(10) 1.538(8), C(10)−C(11) 1.515(8), C(11)−N(12) 1.479(7), N(6)−P(1) 1.799(5), N(12)−P(1) 1.796(5), P(1)−N(13) 1.623(5), As(2)−Cl(4) 2.255(1), As(2)−Cl(5) 2.218(1), As(2)−Cl(6) 2.217(1), As(2)−Cl(2) 2.969(1), As(2)−Cl(3) 3.001(2), As(2)−Cl(1) 3.125(1), Cl(1)−As(1)−Cl(3) 172.5(1), N(2)−As(1)−Cl(2) 171.9(1), N(8)−As(1)−Cl(2′) 174.0(1), Cl(5)−As(2)−Cl(2) 166.6(1), Cl(4)−As(2)−Cl(3) 171.4(1), Cl(6)−As(2)−Cl(1′) 173.7(1).

Å) is nearly perpendicular to the ECl_3 framework and somewhat shorter than the second one (**9** Sb1−N8 2.375 Å; **10·AsCl$_3$** As1−N2 2.012 Å) which shows nearly parallel alignment with the M−Cl bond forming the vertical bar of the T. Two of these primary units associate further via a pair of unsymmetrical chloride bridges to give centrosymmetric dimers with a coordination number of six at the metal atoms (Figure 3). The molecular structure of **10·AsCl$_3$** is completed by capping the central core with the As-atoms of two more molecules of $AsCl_3$, each of which engages in the formation of three halide bridges and attains thus likewise a coordination number of six (Figure 4). Neglecting the large differences in the distances of primary and secondary bonds, the coordination geometry of both types of As-atoms in **10·AsCl$_3$** can be described as octahedral, and the lone-pairs at both centers can be considered stereochemically inactive. The Sb-atoms in **9** interact with two "axial" (Cl1 and Cl2) and four "equatorial" donor atoms (Cl3, N2, N8, and Cl1′ from the second molecule in the dimeric unit) which lie in a common plane which is perpendicular to the axis. The distinct deviation of the axis from linearity (Cl1−Sb1−Cl2 164°) and the irregular distribution of bond angles in the equatorial plane (the Cl3−Sb1−Cl1′ angle of 122.0° is much larger than the remaining three angles, which range from 73.7 to 79.7°) suggest that the lone-pairs at the central atoms are in this case stereochemically active and the coordination can be described as ψ-pentagonal-bipyramidal.

The metal coordination environment of **9** resembles that in the known $SbCl_3$−bipyridine adduct **11**[38] (Chart 2) where the observed (5 + 1) coordination at the antimony atom results likewise from formation of intermolecular chloride bridges, and in complex **12**,[39] where a remote pyridyl group acts as intramolecular secondary ligand; analogous structures have also been observed for complexes $[E_2X_6(LL)_2]$[40] (E = Sb, Bi; X = Br, I; LL = bidentate diphosphine or diarsine ligand). A surprising difference is revealed, however, if one compares the molecular structures of **9** (and **11**) with those of the chemically closely related imine complexes **13**[41] and **14**[42,43] (where a further secondary interaction is blocked by the sterically

Chart 2



demanding ligand and the metal atom remains five-coordinate), as the three chloride ligands feature in this case a facial rather than a meridional arrangement. It is currently not known which factors control the preference for a particular stereoisomer.

The octahedral (3 + 3) coordination of the As(2) atoms in **10·AsCl$_3$** has precedence in the structures of salts containing the complex chloroarsenate ion $[Cl_3As(\mu\text{-}Cl)_3AsCl_3]^{3-}$.[44−46] We are not aware of any isolable diimine complexes of $AsCl_3$, although instable specimens of this type are presumably intermediates during reactions of $AsCl_3$ with bi- and tridentate imines and a suitable reducing agent to give N-heterocyclic arsines or complex As(I) compounds, respectively.[47,48]

The conformation of the heterocyclic diimine ligands in **9** and **10·AsCl$_3$** is at first glance similar to that in **7**, **8**. A closer look reveals, however, that N- and P-bound ligands differ not only in the cisoid rather than transoid arrangement of the "flaps" of the two envelope shaped six-membered rings but show also some significant deviations in bond distances. The carbon−nitrogen distances in the amidine units of P-bound ligands are similar as in diazaphospholidine−4,5-diimines **2a,b**[8,9] and fall into two clearly separated ranges, thus allowing to localize "amine" bonds with prevalent single bond character

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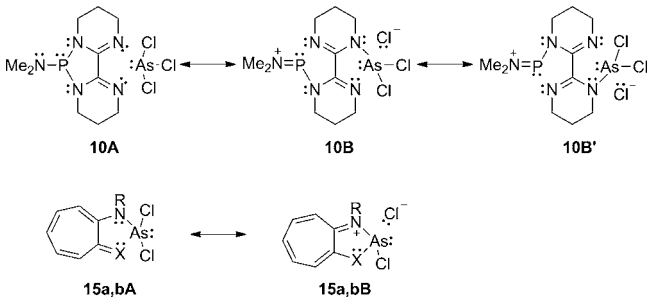
(C−N 1.36−1.42 Å), and "imine" bonds with prevalent double bond character (C═N 1.24−1.30 Å). Comparable values were also observed for the N,N′-bound ligands in transition metal complexes of **2a,b**,[9] whereas complexes [(**2b**)$SnCl_4$][9] and **9** reveal some equalization of amine (1.328−1.350 Å) and imine bonds (1.287−1.298 Å), and both types of bonds become finally indistinguishable within experimental error in **10·$AsCl_3$** (1.303 and 1.308 for amine vs 1.313 and 1.320 Å for imine bonds). At the same time, the C−C bonds connecting the two amidine units shorten slightly from 1.48−1.52 Å in **2a,b** and the P-coordinated ligands in **7**, **8** and 1.469 Å in **9** to 1.454 Å in **10·$AsCl_3$**, and the P−N distances increase from 1.70−1.73 Å in **2a,b** and **7**, **8** via approximately 1.76 Å in **9** and 1.78 Å in **10·$AsCl_3$**. Along with the observation that one of the three "intramolecular" As−Cl bonds (As1−Cl1 2.323 Å) is much shorter than the other two (As1−Cl2 2.779 Å, As1−Cl3 2.713 Å), this trend may be interpreted that the bonding in a monomeric fragment **10** is characterized by a significant contribution of ionic canonical structures **10B**/**10B′** (Scheme 2). A similar situation has previously been encountered in As-

Scheme 2[a]



[a]R = 2,6-*i*$Pr_2C_6H_3$, X = O (**15a**), NR (**15b**).

troponato- and troponimidato complexes **15a,b** where it had also been shown that the loosely bound chloride ligand may easily be abstracted by a suitable Lewis acid to yield intramolecularly donor-stabilized arsenium cations.[49]

The formation of complexes **9**, **10**, and **10·$AsCl_3$** provides not only a proof-of-principle for the Lewis base activity of the diimine unit in **4a** but reveals also that the employed pnictogen chlorides exhibit a specific preference for this site, avoiding P-coordination even when an excess of the Lewis acid is present. In contrast to the diazaphospholidine−diimines **2a,b**, which bind to metals exclusively through the diimine ligands,[9] **4a** displays thus indeed a dual functionality which can be addressed by the electronic demand of the reaction partner: binding at phosphorus prevails for low valent transition metal centers with some degree of back-donation capacity, whereas "pure" Lewis acids with medium to strong electrophilicity interact with the diimine unit. The preference for metathesis over complexation in the reaction with PCl_3 is presumably attributable to the fact that incorporation of another relatively small phosphorus atom (covalent radius 1.07 Å compared to 1.19 Å for As and 1.39 Å for Sb[50]) into the bicyclic structure of a complex induces a high degree of steric strain and renders the product unstable. The failure to observe any complexes featuring bridging 1κP,2κ^2(N,N′)-coordination of **4a** to two like metal centers suggests that—as in **2a,b**—structural and electronic distortions associated with the first complexation step may deactivate the remaining donor site.[51] The observed strongly distorted coordination sphere of the imine-bound As-atom in **10·$AsCl_3$** suggested further that the $AsCl_3$ complex might allow easy reductive generation of a transient As(I) species whose immediate trapping in a [4 + 1] cycloaddition with the diimine[47,48] would offer access to a bicyclic system with As,P-heteropentalene structure.[52]

Both the behavior of **4a** as substrate selective, ambident ligand and the hypothesis of metal binding at one site resulting in a deactivation of the opposite coordination site was confirmed by DFT studies (details are given in the Experimental Section, and a full listing of results is included as Supporting Information). Inspection of the Kohn−Sham (KS) orbitals of the *cisoid* conformers of **4a,b** (the *transoid* isomers display very similar energies and electronic structures but their lower molecular symmetry renders the analysis more intricate) allows us to identify the highest occupied KS orbital (HOMO) in both molecules as a π-orbital which is centered in the oxalamidine unit and must be considered coordination chemically inactive. The HOMO − 1 of **4b** displays contributions from the (σ-type) lone-pairs at phosphorus and the diimine nitrogen atoms (and a chlorine-centered p-orbital; see Figure 5), and the two next KS orbitals represent essentially the symmetrical (n_+) and antisymmetrical (n_-) linear combinations of the lone-pairs at the diimine nitrogen atoms. The formal replacement of a P-chloro by a P-dimethylamino substituent in **4a** raises all KS orbitals in the vicinity of the HOMO by approximately 0.5−0.7 eV and induces a shift in the composition of the HOMO − 1, which represents now essentially a combination of an oxalamidine-centered π-orbital and the phosphorus lone-pair (Figure 5). At the same time, the energetic separation between this orbital and the lone-pairs at the diimine nitrogen atoms (HOMO − 2/HOMO − 3) increases. Inspection of the electrostatic potential reveals a strong concentration of negative charge density in the region of

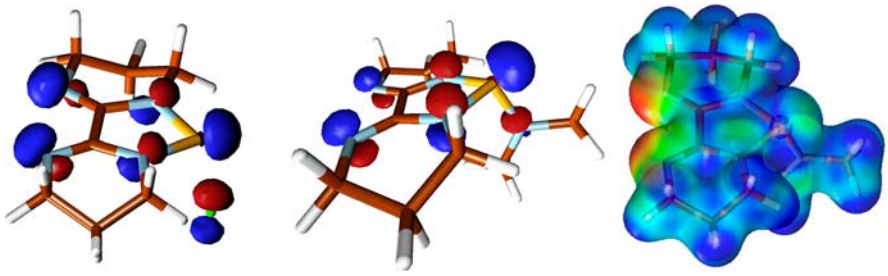


Figure 5. Isodensity representation (isodensity value of 0.08 au) of the energetically second highest KS orbitals (HOMO − 1) of **4b** (left) and **4a** (middle), and isodensity surface with the electrostatic potential for **4a** (right; negative potential encoded in red and positive potentials in blue). All values were calculated at the B3lyp/cc-pVTZ//B3lyp/cc-pVDZ level of theory.

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the diimine donor site whereas the remaining part of the molecule appears rather unpolar (Figure 5). All features together indicate that the presence of the P-NMe_2 substituent makes **4a** a generally stronger donor than **4b**, and attack of a metal substrate on **4a** should occur at the phosphorus lone-pair if the interaction is orbital controlled, and at the diimine unit if the interaction is charge controlled.

In agreement with these assumptions, the calculations predict that a complex [(κP-**4a**)$W(CO)_5$] (**7**) formed by attack of a tungsten carbonyl fragment at the phosphorus donor site of **4a** is in fact by 6.1 kcal mol^{-1} more stable than the appropriate diimine complex [(κ^2-N,N′-**4a**)$W(CO)_4$] and a molecule of CO. Analysis of the KS orbitals of both complexes reveals that metal binding at the phosphorus atom stabilizes the orbitals with significant diimine-lone-pair character (HOMO − 4 and HOMO − 5 in **7**) by approximately 0.4−0.5 eV with respect to free **4a**, whereas attachment of a $W(CO)_4$ moiety to the diimine unit results in an even more pronounced stabilization of the phosphorus lone-pair in [(κ^2-N,N′-**4a**)$W(CO)_4$] (the first orbital showing significant n(P) character is the HOMO − 4 at −7.45 eV, which is by 1.4 eV lower in energy than the corresponding orbital in **4a**).[53] Similar analysis of the appropriate adducts of **4a** with $AsCl_3$ reveals that a species [(κP-**4a**)$AsCl_3$] is best formulated as an unstable adduct which is held together by weak dipole forces (the energy optimized structure is distinguished by a large P···As distance of 3.48 Å close to the sum of van-der-Waals radii and the lack of any significant orbital overlap between the ligand and the $AsCl_3$ fragment) and is, by 7.5 kcal mol^{-1}, less stable than the isomeric [(κ^2-N,N′-**4a**)$AsCl_3$] (**10**). The energy of the first KS orbital of **10** with significant n(P) character (HOMO − 11 at −9.16 eV) is by some 3 eV lower than in **4a**, indicating that the energetic effect of the metal coordination on the phosphorus lone-pair is still larger than in the tungsten complexes, and potential binding of a second metal at this site is therefore out of reach.

CONCLUSIONS

A 1,3,2-diazaphospholidine−4,5-diimine **4a** with tricyclic molecular backbone, which enforces an open conformation of the diimine unit, has been synthesized by transamination of octahydro-2,2′-bipyrimidine with $P(NMe_2)_3$. The reactivity toward selected low valent transition metal carbonyl complexes and main group element halides allows to classify **4a** as ambident ligand which offers dual functionality: coordination to low valent transition metal centers with some capacity for back-donation occurs specifically through the lone-pair at phosphorus whereas pure Lewis acids like pnictogen halides bind exclusively via the diimine unit. This behavior contrasts that of known P-chloro- and P-phenyl-diazaphospholidine-diimines[9] which are one-sided ligands and interact with all Lewis-acids exclusively through the nitrogen lone-pairs. The two-faced reactivity of **4a** is consistently explained by the results of DFT studies: introduction of a P-dimethylamino substituent implies a change in the composition of the KS orbitals which is predicted to favor bonding of a metal fragment through the phosphorus lone-pair if the interaction is orbital-controlled and interaction with the diimine unit if the reaction proceeds under charge control. Metal coordination at either position further shifts the donor orbitals at the remote site to lower energy. As this effect renders the binding of a second metal energetically unfavorable, it provides a plausible explanation for the remarkable tendency of **4a** to avoid formation of dinuclear complexes with simultaneous occupation of both binding sites. Even if this finding discourages the use as a true Janus-faced ligand which can accommodate two metal atoms in close spatial proximity, the proven ability to provide different functionalities for different substrates as well as the additional prospect to exploit a possible redox activity of the diimine unit makes **4a** and other P-amino-1,3,2-diazaphospholidine−4,5-diimines still an interesting ligand system for future studies in coordination chemistry and catalysis.

ASSOCIATED CONTENT

Supporting Information

Full crystallographic data for **7**−**9** and **10**·$AsCl_3$ as CIF, computed coordinates, total energies, and energies of selected KS orbitals for **4a**,**b**, **7**, **10**, [(κ^2-N,N′-**4a**)$W(CO)_4$], [(κP-**4a**)$AsCl_3$], and graphical representations of selected KS orbitals of **4a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(51) In order to establish if a similar deactivating effect operates likewise for a reaction of **4a** with two electrophiles of different type, we reacted cobalt complex **7** with an equimolar amount of $AsCl_3$. CP/MAS NMR spectroscopic analysis of the resulting insoluble material revealed the presence of a mixture of several reaction products. As neither of these could be isolated in pure form or unambiguously identified, the outcome of this experiment remains inconclusive.
(52) Reacting **10** with $SnCl_2$ under similar conditions as had been published previously,[47,48] we obtained an insoluble product whose analytical and spectroscopic data are compatible with a composition [(**4a**)$AsCl_5Sn$]. However, as the spectroscopic data allowed no unambiguous structural assignment and crystallographic characterization was as yet unfeasible, identification of this species requires further efforts.
(53) A hint to the energetics of the formation of dinuclear complexes with **4a** was obtained from a preliminary computational study of the ligand redistribution reaction [(**4a**-κ^2N,N')$W(CO)_4$] + [(**4a**-κ^1P)$W(CO)_5$] ⇆ **4a** + [$(CO)_5W(\mu$-**4a**-$1\kappa^1P$:$2\kappa^2$N,N′)$W(CO)_4$]. The computed reaction energy of +3.4 kcal mol^{-1} at b3lyp/cc-pVTZ(-PP)//b3lyp/cc-pVDZ(-PP) level implies that binding of a second metal to **4a** is in fact energetically disfavored.
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