This article is published as part of the Dalton Transactions themed issue entitled:

New Horizons in Organo-f-element Chemistry

Guest Editor: Geoff Cloke University of Sussex, UK

Published in issue 29, 2010 of Dalton Transactions



Image reproduced with the permission of Tobin Marks

Articles in the issue include:

PERSPECTIVES:

Organo-f-element catalysts for efficient and highly selective hydroalkoxylation and hydrothiolation Charles J. Weiss and Tobin J. Marks, *Dalton Trans.*, 2010, DOI: 10.1039/c003089a

Non-classical divalent lanthanide complexes François Nief, *Dalton Trans.*, 2010, DOI: 10.1039/c001280g

COMMUNICATIONS:

<u>A bimetallic uranium μ -dicarbide complex: synthesis, X-ray crystal structure, and bonding</u> Alexander R. Fox, Sidney E. Creutz and Christopher C. Cummins *Dalton Trans.*, 2010, DOI: 10.1039/c0dt00419g

PAPERS:

Coordination polymerization of renewable butyrolactone-based vinyl monomers by lanthanide and early metal catalysts

Garret M. Miyake, Stacie E. Newton, Wesley R. Mariott and Eugene Y.-X. Chen, *Dalton Trans.*, 2010, DOI: 10.1039/c001909g

Visit the Dalton Transactions website for more cutting-edge inorganic and organometallic chemistry research www.rsc.org/dalton

Neodymium(III) phosphinidene complexes supported by pentamethylcyclopentadienyl and hydrotris(pyrazolyl)borate ligands†

Peng Cui,^{*a*} Yaofeng Chen^{**a*} and Maxim V. Borzov^{*b*}

Received 27th January 2010, Accepted 15th June 2010 First published as an Advance Article on the web 28th June 2010 DOI: 10.1039/C001839B

Synthesis of new neodymium(III) phosphinidene complexes from a neodymium(III) phosphinidene iodide [(μ -PC₆H₃-2,6-^{*i*}Pr₂)Nd(1)(THF)₃]₂ (1) was studied. The metathesis reaction of 1 with KC₅Me₅ (KCp*) gave a neodymium(III) pentamethylcyclopentadienyl phosphinidene complex [(μ -PC₆H₃-2,6-^{*i*}Pr₂)(C₅Me₅)Nd(THF)]₂ (2), and that with potassium hydrotris(pyrazolyl)borate KHB(3-phenylpz)₃ (KTp^{Ph}) generated a neodymium(III) hydrotris(pyrazolyl)borate phosphinidene complex [(μ -PC₆H₃-2,6-^{*i*}Pr₂)(Tp^{Ph*})Nd(THF)]₂ (3) and a C–H bond activation byproduct [κ^4 (N,N',N'',C^{Ph})-Tp^{Ph}]Tp^{Ph}Nd (4). Complexes 2–4 have been characterized by single-crystal X-ray diffraction analysis.

Introduction

Alkyl, amide, and phosphide complexes of lanthanide metals have been extensively explored during the last three decades. These complexes have diverse coordinating properties and reactivities,¹⁻³ and have been widely used in organic⁴ and polymer syntheses.^{5,6} However, chemistry of their counterparts, the alkylidene, imido, and phosphinidene complexes are in their infancy. On the other hand, the alkylidene, imido, and phosphinidene complexes of other early transition metals have received great attention in recent years, and studies on them have revealed their rich coordination chemistry and reactivities.⁷⁻⁹ The scarcity of the alkylidene, imido, and phosphinidene complexes of lanthanide metals is due to the relative mismatch in LUMO/HOMO orbital energy between the Ln^{3+} (d⁰) ions and the alkylidene (imido, or phosphinidene) groups and the lack of synthetic approaches towards these complexes.10 Up until now, only a few examples of lanthanide alkylidene¹¹ and imido¹² complexes have been reported, and the lanthanide phosphinidene complexes are even more sparse. Only two examples of lanthanide phosphinidene complexes have been reported to date. Kiplinger and coworkers reported a late lanthanide Lu(III) phosphinidene complex [{2- $(R_2P)C_6H_4$ ₂NLu(μ -PMes)]₂,¹³ which was prepared by α -hydrogen abstraction of $\{2-(R_2P)C_6H_4\}_2NLu(CH_2SiMe_3)_2$ with MesPH₂ at 80 °C, and our group reported an early lanthanide Nd(III) phosphinidene complex $[(\mu - PC_6H_3 - 2, 6^{-i}Pr_2)Nd(I)(THF)_3]_2$ (1),¹⁴ which was obtained by reaction of $NdI_3(THF)_{3.5}$ with $K[(2,6-{}^{i}Pr_2) C_6H_3PSiMe_3$ via a silyl-group exchange. Because 1 possesses a Nd-I bond, it can serve as a suitable synthetic precursor of other Nd(III) phosphinidene complexes simply via metathesis reactions.

Herein, we report the preparation of Nd(III) phosphinidene complexes supported by pentamethylcyclopentadienyl (Cp*) and hydrotris(pyrazolyl)borate (Tp) ligands obtained from 1 along with the crystal structures of the corresponding metal complexes.

Results and discussion

At first, the metathesis reaction of 1 with KC_5Me_5 (KCp*) was studied. The reaction gave the desired complex 2, in which the I ligand in 1 was replaced by Cp* (Scheme 1). Complex 2 is readily soluble in THF, toluene and benzene, and nearly insoluble in hexane.



Scheme 1 Reaction of 1 with KCp*.

The molecular structure of 2 is given in Fig. 1. It presents a centrosymmetric dimer, with the metal atoms bridged by two phosphinidene ligands. Each Nd(III) center in 2 is in a distorted tetrahedron coordination environment (assuming the Cp* ring occupies one coordination site and not considering far Nd-NdA contact, 4.1164(5) Å). The distances from Nd(III) ion to the carbon atoms on the Cp* ring range from 2.691(4) through to 2.784(4) Å, the average distance (2.738(4) Å) being close to the analogous Nd–C distances in $(Cp^*)(\eta-C_5H_4SiMe_3)NdI(py)$ (2.72 Å) and $(Cp^*)NdI_2(py)_3$ (2.76 Å).¹⁵ The Cp*-ring r.m.s. plane through atoms C21-25 and a plane through Nd, P1, NdA, and P1A atoms (denoted as PL1 and PL2, respectively) form a dihedral angle of 38.4(1)°. Similarly to 1, 2 has slightly nonequivalent Nd-P bonds of 2.7456(11) and 2.7827(10) Å, with the average bond distance, 2.764 Å, being close to that in 1 (2.753 \AA) . The phosphorus atom in 2 is somewhat more tetrahedral

[&]quot;State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai, 200032, China. E-mail: yaofchen@mail.sioc.ac.cn; Fax: +86-21-64166128

^bKey Laboratory of Synthetic and Natural Chemistry of the Ministry of Education, College of Chemistry and Material Science, the North-West University of Xi'an, Taibai Bei avenue 229, Xi'an, 710069, Shaanxi prov, China

[†] CCDC reference numbers 763478–763480. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c001839b



Fig. 1 Two views of the molecular structure of 2 with thermal ellipsoids at the 30% probability level. Isopropyl groups at the aryl substituents and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nd–P1 2.7827(10), Nd–P1A 2.7456(11), Nd–NdA 4.1164(5), Nd–O1 2.486(3), Nd–C21 2.714(4), Nd–C22 2.770(4), Nd–C23 2.784(4), Nd–C24 2.732(4), Nd–C25 2.691(4), \angle Nd–P1–NdA 96.25(3), \angle P1–Nd–P1A 83.75(3) \angle C1–P1–Nd 128.82(14), \angle C1–P1–NdA 124.14(13), The 'A' denoted atoms are at the symmetrically equivalent positions (–*x*, –*y*, –*z*).

 $[C1-P1-Nd = 128.82(14)^{\circ}, Nd-P1-NdA = 96.25(3)^{\circ}, C1-P1-NdA = 124.14(13)^{\circ}, \sum = 349.2(3)^{\circ}]$ in comparison to that in **1** ($\sum = 359.1^{\circ}$). The dihedral angle between the Ph-ring r.m.s. plane (atoms C1-6; denoted as PL3) and PL2 (67.1°) is significantly smaller than that in **1** (81.29°), which can be accommodated by a Cp*-*iso*-propyl repulsions. Coordinated THF molecule is disordered between two positions with site occupancy factors (sof-s) of 0.596(14) and 0.404(14). THF-*iso*-propyl repulsions are also significant, which causes considerable deviation of the O1-Nd-NdA-P1 torsion angle (105.8(1)°) from 90°.

Lanthanide complexes with terminal phosphinidene ligands still remain unknown. The hydrotris(pyrazolyl)borate ligands have a protective pocket of varying size and shape,¹⁶ and a crowded ligand of this type could probably force the cleavage of the bis(µphosphinidene) structure and the formation of the lanthanide terminal phosphinidene complex. Thus, the reaction of **1** with potassium hydrotris(pyrazolyl)borate, KHB(3-Bu'pz)₃, in THF was carried out. However, all attempts to obtain any crystalline product from this reaction mixture failed. Application of another hydrotris(pyrazolyl)borate, KHB(3-phenylpz)₃ (KTp^{Ph}), in the same reaction gave complex **3** as dark red crystalline blocks and complex **4** as brown prisms (Scheme 2).

The molecular structures of **3** and **4** are shown in Fig. 2 and 3, respectively. Complex **3** presents a centrosymmetric dimer and retains the bis(μ -phosphinidene)dineodymium structural unit. It crystallizes as a solvate adduct with one molecule of THF which is disordered around the inversion center (0, 1/2, 0) and equivalents (space group $P\bar{1}$). One of the pyrazolyl groups of the



Scheme 2 Reaction of 1 with KTp^{Ph} .

Tp^{Ph} ligand undergoes a "1,2-borotropic" shift to switch the phenyl substituent on it (the C32–37 ring in Fig. 2) from the 3rd to the 5th position to alleviate the steric congestion around the metal center (Scheme 3). Such isomerization of the ligand has been observed in some other pyrazolylborate metal complexes.¹⁷ The Nd(III) center adopts a pseudo-octahedron geometry with two phosphinidene groups and two pyrazolyl groups forming the equatorial plane, and a pyrazolyl group and a THF molecule occupying the apical positions. The distance from the Nd(III) ion to the nitrogen atom of 5-substituted pyrazolyl group is 2.497(5) Å, falling within the



Fig. 2 Two views of the molecular structure of **3** with thermal ellipsoids at the 30% probability level. Isopropyl groups at the aryl substituents and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nd1–P1 2.7808(16), Nd1–P1A 2.7911(15), Nd1–N1 2.714(5), Nd1–N3 2.497(5), Nd1–N5 2.707(5), Nd1–O1 2.460(4), \angle Nd1–P1–Nd1A 103.25(5), \angle P1–Nd–P1A 76.75(5), \angle C1–P1–Nd1 128.01(19), \angle C1–P1–Nd1A 127.67(19), The 'A' denoted atoms are at the symmetrically equivalent positions (2 – x, 2 – y, 1 – z).



Fig. 3 Molecular structure of 4 with thermal ellipsoids at the 30% probability level. Minor component and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) (for only the main of two disordered components): Nd1–N2A 2.868(5), Nd1–N4A 2.564(5), Nd1–N6A 2.529(5), Nd1–N2B 2.487(6), Nd1–N4B 2.722(6), Nd1–N6B 2.646(6), Nd1–C5B 2.569(7).



Scheme 3 Isomerization of Tp^{Ph} ligand via a 1,2-borotropic shift

range of 2.46 to 2.52 Å reported for the less hindered monohydrotris(pyrazolyl)borate Nd(III) complexes.¹⁸ The distances from the Nd(III) ion to the nitrogen atoms on 3-substituted pyrazolyl groups, 2.714(5) Å and 2.707(5) Å, are significantly longer. The same observation was reported for Co(II)[HB(3-ⁱPrpz)₂(5-^{*i*}Prpz)]₂,^{17a} Zn(II)I[HB(3-mesitylpz)₂(5mesitylpz)],^{17c} M(II)[HB(4- $(CN-3-Phpz)_2(4-CN-5-Phpz)_2(M = Mn, Fe, Co)^{17e}$ which can be ascribed to steric effects. Unlike in 1 and 2, 3 has nearly equivalent Nd–P bonds (2.7808(16) and 2.7911(15) Å), and the average bond length (2.786 Å) is slightly longer than those in 1 (2.753 Å) and 2 (2.764 Å). Interestingly, the dihedral angle between the 2,6-(diisopropyl)phenyl ring and the Nd1-P1-Nd1A-P1A plane in $3(50.2^{\circ})$ is much smaller than those in $1(81.3^{\circ})$ and $2(67.1^{\circ})$. The geometry of the phosphorus atom in 3 is very close to trigonal planar (C1-P1-Nd1 = 128.01(19)°, Nd1-P1-Nd1A = 103.25(5)°, $C1-P1-Nd1A = 127.67(19)^{\circ}$, $\Sigma = 358.9(4)^{\circ}$). The Nd-coordinated THF molecule in 3 is disordered between two positions with sof-s 0.47(2) and 0.53(2).

The crystal of 4 is presented by two components with sof-s 0.905(2) and 0.095(2) (only the main of the two disordered components is discussed).[†] In 4, there is a sevencoordinated Nd(III) center bound by one monoanionic hydrotris-(pyrazolyl)borate ligand and one dianionic hydrotris-(pyrazolyl)borate ligand. In the latter one Ph-group orthoproton is removed and the deprotonated Ph-ring becomes σ -bonded to the Nd center. The distances from Nd(III) ion to the nitrogen atoms on the Tp^{Ph} ligands are quite different due to formation of the five member Nd1/N2B/C3B/C4B/C5B metallacycle. The Nd1-N2B bond (2.487(6) Å) is the shortest one, while the Nd1-N4B and Nd1-N6B bonds (2.722(6) and 2.646(6) Å) are longer than the Nd1-N4A and Nd1-N6A ones (2.564(5) and 2.529(5) Å). The Nd1-N2A bond (2.868(5) Å) is noticeably elongated, most likely, due to steric interactions between the phenyl groups. The Nd1-N4A and Nd1-N6A bond lengths are close to those in the less hindered Nd(III) complexes $[Nd(HB(pz)_3)_2Cl(H_2O)] (2.566-2.613 \text{ Å})^{19a}$ and [NdCl(HB(pz)₃)₂(Hpz)] (2.57–2.59 Å).^{19b} Formation of **4** is a result of a rather unusual aromatic o-C-H bond activation. The Nd-C_{Ph} distance of 2.569(7) Å in 4 is close to those in the only reported complex containing σ -Nd–Ph bond [(C₅H₅)₃NdC₆H₅][Li(DME)₃] (2.593(17), 2.613(13) and 2.601(13) Å).²⁰ To the best of our knowledge, 4 represents the first example of C-H bond activation of a Tp^{Ph} ligand for the lanthanide complexes. Similar C-H bond activation at phenyl substituent of Tp^{Ph} ligand has been reported for some transition metal complexes, such as $[Rh(H)(CO){HB(C_3H_2N_2C_6H_3OCH_3)(C_3H_2N_2C_6H_4OCH_3)_2}]^{21a}$ and $[IrHB(C_3H_2N_2C_6H_3)(C_3H_2N_2C_6H_4)_2(H)(=C(CH_2)_3O)]$.^{21b}

Conclusions

Our study demonstrated that new neodymium(III) phosphinidene complexes can be synthesized by using a neodymium(III) phosphinidene iodide $[(\mu-PC_6H_3-2,6-iPr_2)Nd(I)(THF)_3]_2$ (1) as the precursor *via* metathesis reactions. In this way, the lanthanide phosphinidene complexes supported by pentamethylcyclopentadienyl and hydrotris(pyrazolyl)borate ligands, $[(\mu-PC_6H_3-2,6-iPr_2)(C_5Me_5)Nd(THF)]_2$ (2) and $[(\mu-PC_6H_3-2,6-iPr_2)(Tp^{Ph*})Nd(THF)]_2$ (3), have been prepared and structurally characterized. Complexes 2 and 3 both possess the bridging phosphinidene structure, and in 3 one pyrazolyl group of the Tp^{Ph} ligand undergoes a "1,2-borotropic" shift to minimize the steric congestions around the metal center. The lanthanide terminal phosphinidene complex is still not accessible, and the synthesis of this complex is under investigation.

Experimental

General Procedures

All operations were carried out under an atmosphere of argon using Schlenk techniques or in a nitrogen gas filled glovebox. THF was distilled from Na-benzophenone ketyl and degassed prior to use, toluene and hexane were dried over Na/K alloy. C_6D_6 were purchased from Cambridge Isotopes, dried over Na/K

[‡] For model definition, restrains applied, and exhaustive structural discussion of complex **4** including the details of packing, see the corresponding sections of the provided CIF file.

alloy, distilled under vacuum and stored in a glovebox. [(μ -PC₆H₃-2,6-'Pr₂)Nd(I)(THF)₃]₂ (1) was synthesized as we reported previously.¹⁴ KC₅Me₅,²² KHB(3-Bu'pz)₃ and KHB(3-phenylpz)₃²³ were prepared according to the literature procedures. ¹H NMR spectra were recorded on a Varian Mercury 400 spectrometer, chemical shifts were reported in δ (ppm) units with references to the residual solvent resonance of the deuterated solvents. Elemental analyses was performed by Analytical Laboratory of Shanghai Institute of Organic Chemistry.

$[(\mu - PC_6H_3 - 2, 6^{-i}Pr_2)(C_5Me_5)Nd(THF)]_2$ (2)

 KC_5Me_5 (19 mg, 0.10 mmol) and 1 (69 mg, 0.05 mmol) were mixed in 4 mL of toluene. The dark red mixture was stirred overnight at room temperature and filtered. The dark red filtrate was concentrated to approximately 0.5 mL, and then 3 mL of hexane was layered to give 2 as a dark red solid (28 mg, 52% yield). Anal. Calcd for $C_{52}H_{80}Nd_2O_2P_2$: C, 57.42; H, 7.41. Found: C, 54.48; H, 7.06. The found carbon content is somewhat low, the same was also reported for some other lanthanide complexes derived from P-atom-containing ligands.²⁴ The NMR signals are very broad and not informative. The complex is thermal instable in C_6D_6 .

$$\label{eq:constraint} \begin{split} & [(\mu\text{-}PC_6H_3\text{-}2,6\text{-}'Pr_2)(Tp^{Ph*})Nd(THF)]_2 \ (3) \ and \\ & [\kappa^4(N,N',N'',C^{Ph})\text{-}Tp^{Ph}]Tp^{Ph}Nd \ (4) \end{split}$$

KHB(3-phenylpz)₃ (57 mg, 0.118 mmol) and 1 (80 mg, 0.059 mmol) were mixed in 7 mL of THF. The dark red mixture

 Table 1
 Crystal data and refinement parameters for 2–4

was stirred overnight at room temperature. The precipitate was removed by centrifugation. The dark red filtrate was concentrated to approximately 2 mL, and then 9 mL of hexane was layered to give dark-red crystalline blocks of 3 and brown crystalline prisms of 4. The well-formed crystals of 3 and 4 are fine distinguished from each other and were separated manually. The yield of 3 is about 10~15 mg and that of 4 is about 30~40 mg. 3: Anal. Calcd for C₈₆H₉₄B₂N₁₂Nd₂O₂P₂: C, 60.77; H, 5.57; N, 9.89. Found: C, 59.82; H, 5.72; N: 10.10. The NMR signals are very broad and not informative. The complex is thermal instable in C₆D₆. 4: Anal. Calcd for C₅₄H₄₃B₂N₁₂Nd: C, 63.22; H, 4.22; N, 16.38. Found: C, 62.27; H, 4.95; N: 15.98. ¹H NMR (400 MHz, C₆D₆, 25 °C) : δ = 57.61 (bs, 1H), 34.94 (bs, 2H), 25.44 (bs, 1H), 24.19 (s, 1H), 18.45 (bs, 1H), 17.29 (bs, 1H), 15.21 (bs, 1H), 14.77 (bs, 2H), 13.43 (bs, 1H), 12.68 (bs, 1H), 11.55 (bs, 1H), 9.76 (bs, 2H), 7.36 (bs, 3H), 6.96 (bs, 1H), 5.71 (bs, 2H), 4.65 (bs, 3H), 2.84 (bs, 2H), 2.42 (bs, 2H), 1.62 (bs, 2H), 1.24 (bs, 1H), 0.57 (bs, 4H), -0.48 (bs, 4H), -1.78 ppm (bs, 4H).

X-Ray crystallography[†]

Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into toluene (complex 2) or THF (complexes 3 and 4) solutions, mounted under argon in thin-walled glass capillaries that were sealed off. Data collection were performed on a Bruker SMART diffractometer (graphite-monochromatized Mo-K α radiation, 0.71073 Å) using ω scan mode at 20(2) °C. The

	2	3	4
Empirical formula	$C_{52}H_{80}Nd_2O_2P_2$	$C_{86}H_{94}B_2N_{12}Nd_2O_2P_2\cdot C_4H_8O$	$C_{54}H_{43}B_2N_{12}Nd$
Formula weight	1087.58	1771.88	1025.86
Colour, habit	Red block	Red block	Brown prism
Crystal size/mm	$0.30 \times 0.21 \times 0.16$	$0.36 \times 0.34 \times 0.26$	$0.38 \times 0.25 \times 0.19$
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\overline{1}$	$P2_1/c$
Cell dimensions			
a/Å	11.3913(10)	11.9838(16)	11.719(2)
b/Å	18.0366(16)	14.2191(19)	18.458(3)
c/Å	12.6070(11)	14.739(2)	21.719(4)
$\alpha/^{\circ}$	90	98.263(2)	90
$\beta/^{\circ}$	97.184(2)	109.668(2)	94.824(4)
$\gamma/^{\circ}$	90	109.723(2)	90
$V/Å^3$	2569.9(4)	2130.4(5)	4681.4(15)
Ζ	2	1	4
Density (calc.)/g cm^{-3}	1.405	1.381	1.456
Absorption coeff./mm ⁻¹	2.10	1.30	1.16
F(000)	1116	910	2084
Min./max. transmission	0.572/0.730	0.652/0.729	0.667/0.810
θ range/	1.98 - 25.10	1.86 - 25.10	1.88 - 25.10
Index ranges	$-13 \le h \le 13$	$-14 \le h \le 14$	$-13 \le h \le 13$
	$-21 \le k \le 18$	$-16 \le k \le 13$	$-22 \le k \le 19$
	$-14 \le l \le 15$	$-16 \le l \le 17$	$-18 \le l \le 25$
Reflections collected	12923	10502	23265
Independent reflections (R_{int})	4570 (0.0286)	7428 (0.0375)	8312 (0.0633)
Reflections with $I > 2\sigma(I)$	3961	5860	6023
Data/restraints/parameters	4570/79/290	7428/159/550	8312/720/904
Goodness of fit	1.06	0.98	1.07
<i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0347$	$R_1 = 0.0535$	$R_1 = 0.0613$
	$wR_2 = 0.0813$	$\dot{W}R_{2} = 0.1179$	$wR_2 = 0.1323$
R indices (all data)	$R_1 = 0.0415$	$R_1 = 0.0727$	$R_1 = 0.0905$
	$wR_2 = 0.0841$	$wR_2 = 0.1247$	$WR_2 = 0.1416$
Completeness to $\theta = 25.1^{\circ}$	99 .8%	97. <u>9</u> %	99.8
Largest diff. peak/hole/e Å ⁻³)	0.71/-0.67	1.43/-0.79	1.51/-1.05

SMART program package²⁵ was used to determine the unit-cell parameters. Data reduction were performed with the *SAINT*+ program package.²⁶ In all cases, the absorption corrections were performed semi-empirically from equivalents.²⁷ The structures were solved by direct methods and refined on F^2 by full-matrix least squares techniques with anisotropic thermal parameters for non-hydrogen atoms.²⁸ H-atoms, except BH in **3** and **4**, were placed at calculated positions and refined isotropically using the riding model. Borohydride H-atoms in **3** and **4** were found from difference Fourier synthesis and refined isotropically. Details on the restrains applied can be found in the ESII (corresponding sections of CIF files for complexes **2–4**).[†] Crystal data and refinement parameters for **2–4** are listed in Table 1.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 20872164 and 20821002), and Chinese Academy of Sciences.

Notes and references

- 1 H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95**, 865.
- 2 (a) F. T. Edelmann, D. M. M. Freckmann and H. Schumann, *Chem. Rev.*, 2002, **102**, 1851; (b) S. Arndt and J. Okuda, *Chem. Rev.*, 2002, **102**, 1953.
- 3 (a) W. J. Evans, I Bloom, W. E. Hunter and J. L. Atwood, Organometallics, 1983, 2, 709; (b) H. Schumann, E. Palamidis, G. Schmid and R. Boese, Angew. Chem., Int. Ed. Engl., 1986, 25, 718; (c) H. C. Aspinall, S. R. Moore and A. K. Smith, J. Chem. Soc., Dalton Trans., 1992, 153; (d) W. Clegg, K. Izod, S. T. Liddle, P. O'Shaughnessy and J. M. Sheffield, Organometallics, 2000, 19, 2090; (e) G. W. Rabe, J. Riede and A. Schier, Inorg. Chem., 1996, 35, 40; (f) G. W. Rabe and J. W. Ziller, Inorg. Chem., 1995, 34, 5378; (g) G. W. Rabe, G. P. A. Yap and A. L. Rheingold, Inorg. Chem., 1995, 34, 4521; (h) F. Nief and L. Ricard, J. Organomet. Chem., 1997, 529, 357.
- 4 (a) S. Hong and T. J. Marks, Acc. Chem. Res., 2004, **37**, 673; (b) G. A. Molander and J. A. C. Romero, Chem. Rev., 2002, **102**, 2161.
- 5 (a) H. Yasuda, J. Organomet. Chem., 2002, 647, 128; (b) Z. Hou and Y. Wakatsuki, Coord. Chem. Rev., 2002, 231, 1.
- 6 (a) S. B. Amin and T. J. Marks, Angew. Chem., Int. Ed., 2008, 47, 2006; (b) J. Gromada, J. F. Carpentier and A. Mortreux, Coord. Chem. Rev., 2004, 248, 397.
- 7 (a) R. R. Schrock, *Chem. Rev.*, 2002, **102**, 145; (b) R. R. Schrock, *Chem. Rev.*, 2009, **109**, 3211; (c) J. W. Herdon, *Coord. Chem. Rev.*, 2010, **1-2**, 103.
- 8 (a) A. P. Duncan and R. G. Bergman, *Chem. Rec.*, 2002, 2, 431; (b) L. H. Gade and P. Mountford, *Coord. Chem. Rev.*, 2001, 216–217, 65; (c) N. Hazari and P. Mountford, *Acc. Chem. Res.*, 2005, 38, 839; (d) D. J. Mindiola, *Acc. Chem. Res.*, 2006, 39, 813.
- 9 (a) A. H. Cowley, Acc. Chem. Res., 1997, **30**, 445; (b) D. W. Stephan, Angew. Chem., Int. Ed., 2000, **39**, 314; (c) F. Mathey, Angew. Chem., Int. Ed., 2003, **42**, 1578; (d) K. Lammertsma, Top. Curr. Chem., 2003, **229**, 95.
- 10 G. R. Giesbrecht and J. C. Gordon, Dalton Trans., 2004, 2387.
- 11 (a) H. Schumann and J. Müller, J. Organomet. Chem., 1979, 169, C1;
 (b) K. Aparna, M. Ferguson and R. G. Cavell, J. Am. Chem. Soc., 2000,
 122, 726; (c) R. G. Cavell, R. P. K. Babu and K. Aparna, J. Organomet. Chem., 2001, 617, 158; (d) T. Cantat, F. Jaroschik, F. Nief, L. Ricard,
 N. Mézailles and P. L. Floch, Chem. Commun., 2005, 5178; (e) T.
 Cantat, F. Jaroschik, L. Ricard, P. L. Floch, F. Nief and N. Mézailles,

Organometallics, 2006, 25, 1329; (f) S. T. Liddle, J. McMastera, J. C. Green and P. L. Arnold, Chem. Commun., 2008, 1747; (g) D. P. Mills, O. J. Cooper, J. McMaster, W. Lewis and S. T. Liddle, Dalton Trans., 2009, 4547; (h) D. P. Mills, A. J. Wooles, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, Organometallics, 2009, 28, 6771; (i) H. M. Dietrich, K. W. Törnroos and R. Anwander, J. Am. Chem. Soc., 2006, 128, 9298; (j) M. Zimmermann, J. Takats, G. Kiel, K. W. Törnroos and R. Anwander, Chem. Commun., 2008, 612; (k) R. Litlabø, M. Zimmermann, K. Saliu, J. Takats, K. W. Törnroos and R. Anwander, Angew. Chem., Int. Ed., 2008, 47, 9560; (l) J. Scott, H. J. Fan, B. F. Wicker, A. R. fout, M. H. Baik and D. J. Mindiola, J. Am. Chem. Soc., 2008, 130, 14438.

- 12 (a) A. A. Trifonov, M. N. Bochkarev, H. Schumann and J. Loebel, Angew. Chem., Int. Ed. Engl., 1991, 30, 1149; (b) Z. W. Xie, S. W. Wang, Q. C. Yang and T. C. W. Mak, Organometallics, 1999, 18, 1578; (c) S. W. Wang, Q. C. Yang, T. C. W. Mak and Z. W. Xie, Organometallics, 1999, 18, 5511; (d) H. S. Chan, H. W. Li and Z. W. Xie, Chem. Commun., 2002, 652; (e) J. C. Gordon, G. R. Giesbrecht, D. L. Clark, P. J. Hay, D. W. Keogh, R. Poli, B. L. Scott and J. G. Watkin, Organometallics, 2002, 21, 4726; (f) D. J. Beetstra, A. Meetsma, B. Hessen and J. H. Teuben, Organometallics, 2003, 22, 4372; (g) A. G. Avent, P. B. Hitchcock, A. V. Khvostov, M. F. Lappert and A. V. Protchenko, Dalton Trans., 2004, 2272; (h) D. M. Cui, M. Nishiura and Z. M. Hou, Angew. Chem., Int. Ed., 2005, 44, 959; (i) J. Scott, F. Basuli, A. R. Fout, J. C. Huffman and D. J. Mindiola, Angew. Chem., Int. Ed., 2008, 47, 8502; (j) C. L. Pan, W. Chen, S. Y. Song, H. J. Zhang and X. W. Li, Inorg. Chem., 2009, 48, 6344.
- 13 J. D. Masuda, K. C. Jantunen, O. V. Ozerov, K. J. T. Noonan, D. P. Gates, B. L. Scott and J. L. Kiplinger, J. Am. Chem. Soc., 2008, 130, 2408.
- 14 P. Cui, Y. F. Chen, X. Xu and J. Sun, Chem. Commun., 2008, 5547.
- 15 D. L. Clark, J. C. Gordon, B. L. Scott and J. G. Watkin, *Polyhedron*, 1999, **18**, 1389.
- 16 (a) S. Trofimenko, Chem. Rev., 1993, 93, 943; (b) N. Marques, A. Sella and J. Takats, Chem. Rev., 2002, 102, 2137.
- 17 (a) S. Trofimenko, J. C. Calabrese, P. J. Domaille and J. S. Thompson, *Inorg. Chem.*, 1989, 28, 1091; (b) M. Cano, J. V. Heras, S. Trofimenko, A. Monge, E. Gutierrez, C. J. Jones and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1990, 3577; (c) A. L. Rheingold, C. B. White and S. Trofimenko, *Inorg. Chem.*, 1993, 32, 3471; (d) M. H. Chisholm, N. W. Eilerts and J. C. Huffman, *Inorg. Chem.*, 1996, 35, 445; (e) N. F. Zhao, M. J. Van Stipdonk, C. Bauer, C. Campana and D. M. Eichhorn, *Inorg. Chem.*, 2007, 46, 8662.
- 18 D. P. Long, A. Chandrasekaren, R. O. Day, P. A. Bianconi and A. L. Rheingold, *Inorg. Chem.*, 2000, **39**, 4476.
- 19 (a) C. D. Sun and W. K. Wong, *Inorg. Chim. Acta*, 1997, **255**, 355; (b) M. Onishi, N. Nagaoka, K. Hiraki and K. Itoh, *J. Alloys Compd.*, 1996, **236**, 6.
- 20 H. R. Gao, Q. Shem, J. Y. Hu, S. C. Jin and Y. H. Lin, J. Organomet. Chem., 1992, 427, 141.
- 21 (a) M. D. Santa María, R. M. Claramunt, J. A. Campo, M. Cano, R. Criado, J. V. Heras, P. Ovejero, E. Pinilla and M. R. Torres, J. Organomet. Chem., 2000, 605, 117; (b) C. Slugovc, K. Mereiter, S. Trofimenko and E. Carmona, Angew. Chem., Int. Ed., 2000, 39, 2158.
- 22 G. Rabe, H. W. Roesky, D. Stalke, F. Pauer and G. M. Sheldrick, J. Organomet. Chem., 1991, 403, 11.
- 23 D. M. Eichhorn and W. H. Armstrong, Inorg. Chem., 1990, 29, 3607.
- 24 T. Gröb, G. Seybert, W. Massa, F. Weller, R. Palaniswami, A. Greiner and K. Dehnicke, *Angew. Chem., Int. Ed.*, 2000, **39**, 4373.
- 25 SMART Version 5.628, Bruker Asx Inc.
- 26 SAINT + Version 6.22a, Bruker Axs Inc.
- 27 G. M. Sheldrick, SADABS, Program for area detector adsorption correction, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.
- 28 G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997; G. M. Sheldrick, SHELXS-97, Program for solution of crystal structures, University of Göttingen, Germany, 1997.