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Synthesis, Structures, and Reactivity of Yttrium Alkyl and Alkynyl Complexes with Mixed Tp^{Me2}/Cp Ligands

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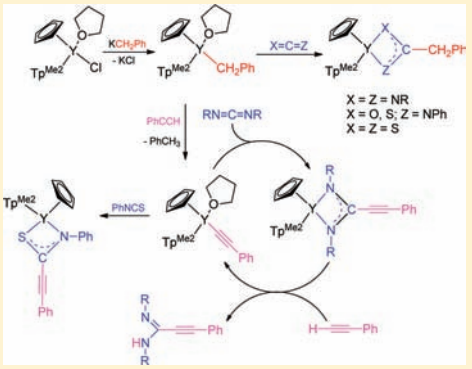
Supporting Information

ABSTRACT: The structurally characterized Tp^{Me2}-supported rare earth metal monoalkyl complex $(Tp^{Me2})CpYCH_2Ph(THF)$ (**1**) was synthesized via the salt-metathesis reaction of $(Tp^{Me2})CpYCl(THF)$ with KCH_2Ph in THF at room temperature. Treatment of **1** with 1 equiv of PhC≡CH under the same conditions afforded the corresponding alkynyl complex $(Tp^{Me2})CpYC{\equiv}CPh(THF)$ (**2**). Complex **1** exhibits high activity toward carbodiimides, isocyanate, isothiocyanate, and CS_2; treatment of **1** with such substrates led to the formation of a series of the corresponding Y−C(benzyl) σ-bond insertion products $(Tp^{Me2})CpY[(RN)_2CCH_2Ph]$ (R = ^{i}Pr(**3a**), Cy(**3b**), 2,6-^{i}Pr−C_6H_3(**3c**)), $(Tp^{Me2})CpY[SC(CH_2Ph)NPh]$ (**4**), $(Tp^{Me2})CpY[OC(CH_2Ph)NPh]$ (**5**), and $(Tp^{Me2})CpY(S_2CCH_2Ph)$ (**6**) in 40−70% isolated yields. Carbodiimides and isothiocyanate can also insert into the Y−C(alkynyl) σ bond of **2** to yield complexes $(Tp^{Me2})CpY[(RN)_2CC{\equiv}CPh]$ (R = ^{i}Pr(**7a**), Cy(**7b**)) and $(Tp^{Me2})CpY[SC(C{\equiv}CPh)NPh]$ (**9**). Further investigation results indicated that **1** can effectively catalyze the cross-coupling reactions of phenylacetylene with carbodiimides. However, treatment of *o*-allylaniline with a catalytic amount of **1** gave only the benzyl abstraction product $(Tp^{Me2})CpY(NHC_6H_4CH_2CH{=}CH_2$-*o*$)(THF)$ (**10**), without observation of the expected organic hydroamination/cyclization product. All of these new complexes were characterized by elemental analysis and spectroscopic properties, and their solid-state structures were also confirmed by single-crystal X-ray diffraction analysis.



INTRODUCTION

The modification of reactivity of metal complexes through the choice of appropriate ancillary ligands is a long-standing research subject in inorganic chemistry and organometallic chemistry.[1,2] Significant efforts have focused on the scorpionate-supported tris(pyrazolyl)borate ligands ($Tp^{R,R'}$), because their steric profiles can be modified by variation of the substituents in the 3 and 5 positions of the pyrazolyl rings. It has been found that this type of ligand can coordinate to metal ions from all parts of the periodic table.[3,4] Pioneer works have been done in basic chemistry of the tris(pyrazolyl)borate lanthanide complexes by Bagnall's and Takats' groups, and many organolanthanide complexes with unique reaction patterns have been synthesized.[5] However, it is usually unsuccessful to attempt to synthesize $Tp^{R,R'}$-supported lanthanide (III) derivatives via salt-metathesis of $Tp^{R,R'}LnCl_2$ or $Tp^{R,R'}{}_2LnCl$ with ML (M = Li or Na) due to the facile occurrence of $Tp^{R,R'}$ ligand-replacement or degradation during these processes.[6] In contrast to organolanthanide complexes featuring the guanidinate and amidinate ligand,[7,8] $Tp^{R,R'}$-supported lanthanide(III) derivatives such as hydride, alkyl, alkynyl, and amide are rare.[9] Recently, we investigated the reaction of Cp_2LnCl with KTp^{Me2} and thus synthesized the mixed Tp^{Me2}/Cp lanthanide chlorides $(Tp^{Me2})CpLnCl(THF)$ (Ln = Y, Yb, Er, Dy) via a cyclopentadienyl-exchange process.[10] Notably, $(Tp^{Me2})CpLnCl(THF)$ is a suitable precursor for the preparation of mixed Tp^{Me2}/Cp lanthanide derivatives by reaction with the corresponding reagents. Herein, we report the synthesis of mixed Tp^{Me2}/Cp yttrium alkyl and alkynyl complexes $(Tp^{Me2})CpYCH_2Ph(THF)$ (**1**) and (Tp^{Me2})-$CpYC{\equiv}CPh(THF)$ (**2**) as well as their reactivities toward a series of unsaturated organic molecules, demonstrating that these small molecules insert readily into the Y−C(alkyl, alkynyl) σ bond of **1** and **2** under mild conditions. Furthermore, we also found that **1** is an excellent catalyst for the cross-coupling reaction of carbodiimides with phenylacetylene.

EXPERIMENTAL SECTION

General Procedure. All operations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified nitrogen using standard Schlenk techniques or a glovebox. The solvents of THF, toluene, and *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. Carbodiimides, phenyl isocyanate, phenyl isothiocyanate, phenylacetylene, and carbon dithioxide were purchased from Aldrich

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Table 1. Crystal and Data Collection Parameters of Complexes 1, 2, and 3a, and 3b

	1	2	3a	3b
formula	$C_{31}H_{42}BN_6OY$	$C_{32}H_{40}BN_6OY$	$C_{34}H_{48}BN_8Y$	$C_{40}H_{56}BN_8Y$
mw	614.43	624.42	668.52	748.65
cryst color	colorless	colorless	colorless	colorless
cryst dimens (mm)	0.25 × 0.20 × 0.15	0.15 × 0.12 × 0.10	0.15 × 0.10 × 0.06	0.25 × 0.10 × 0.05
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$
unit cell dimensions				
a (Å)	18.215(2)	9.8463(19)	12.421(4)	10.710(5)
b (Å)	10.7667(13)	16.590(3)	13.034(4)	10.896(5)
c (Å)	17.888(2)	19.781(4)	13.222(4)	19.137(8)
α (deg)	90.00	90.00	83.886(4)	76.941(6)
β (deg)	118.184(2)	96.128(3)	75.816(4)	75.218(6)
γ (deg)	90.00	90.00	64.566(3)	66.994(5)
V (Å^3)	3092.1(7)	3212.9(11)	1874.2(10)	1967.6(15)
Z	4	4	2	2
D_{calcd} (g cm^{-3})	1.320	1.291	1.185	1.264
μ (mm^{-1})	1.920	1.849	1.588	1.520
F (000)	1288	1304	704	792
radiation (λ = 0.710730 Å)	Mo Kα	Mo Kα	Mo Kα	Mo Kα
temperature (K)	293(2)	293(2)	293(2)	293(2)
scan type	ω-2θ	ω-2θ	ω-2θ	ω-2θ
θ range (deg)	1.27−25.00	2.07−25.01	1.59−25.09	2.05−23.29
h, k, l range	$-21 \le h \le 18$	$-11 \le h \le 6$	$-14 \le h \le 14$	$-11 \le h \le 11$
	$-12 \le k \le 11$	$-19 \le k \le 18$	$-15 \le k \le 14$	$-12 \le k \le 12$
	$-21 \le l \le 20$	$-22 \le l \le 23$	$-15 \le l \le 7$	$-21 \le l \le 14$
no. of reflns measured	12568	15662	7807	6898
no. of unique reflns	5445 [R(int) = 0.0395]	5657 [R(int) = 0.0410]	6509 [R(int) = 0.0251]	5599 [R(int) = 0.0398]
completeness to θ	99.9% (θ = 25.00)	99.8% (θ = 25.01)	97.6% (θ = 25.09)	98.8% (23.29)
max. and min. transmission	0.7617 and 0.6454	0.8367 and 0.7689	0.9107 and 0.7966	0.9278 and 0.7024
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	5445/0/364	5657/1/382	6509/0/400	5599/0/461
goodness-of-fit on F^2	1.037	1.019	0.994	0.907
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0434	R_1 = 0.0441	R_1 = 0.0547	R_1 = 0.0415
	wR_2 = 0.1106	wR_2 = 0.1077	wR_2 = 0.1433	wR_2 = 0.0800
R indices (all data)	R_1 = 0.0716	R_1 = 0.0777	R_1 = 0.0853	R_1 = 0.0686
	wR_2 = 0.1252	wR_2 = 0.1237	wR_2 = 0.1538	wR_2 = 0.0881
largest diff. peak and hole (e Å^{-3})	0.421 and −0.328	0.340 and −0.329	0.498 and −0.429	0.395 and −0.307

and were used without purification. (Tp^{Me2})CpYCl(THF),[10] benzyl potassium,[11a] and *o*-allylaniline[11b] were prepared by slightly modified literature methods. Elemental analyses for C, H, and N were carried out on a Rapid CHN-O analyzer. ^{1}H NMR data were obtained on a Jeol ECA-400 NMR spectrometer (C_6D_6 7.16 ppm).

Synthesis of (Tp^{Me2})CpYCH$_2$Ph(THF) (1). To a THF (30 mL) solution of (Tp^{Me2})CpYCl(THF) (0.559 g, 1.0 mmol) was added solid KCH_2Ph (0.130 g, 1.0 mmol) at room temperature; the mixture was allowed to stir overnight. The pale-white thick solution was evaporated to dryness under vacuum conditions, and to the residue was added toluene (30 mL). After stirring for 30 min, the mixture was filtered through Celite. The filtrate was concentrated to ca. 10 mL and then layered with *n*-hexane to afford **1** as colorless crystals. Yield: 0.509 g (83%). Anal. Calcd for $C_{31}H_{42}BN_6OY$ (614.43): C, 60.60; H, 6.89; N, 13.68. Found: C, 60.42; H, 6.72; N, 13.88. ^{1}H NMR: δ 7.39−7.42 (m, 2H, C_6H_5), 7.30−7.32 (m, 2H, C_6H_5), 6.92−6.96 (m, 1H, C_6H_5), 6.34 (s, 5H, C_5H_5), 5.60 (s, 3H, 4H-Tp^{Me2}), 3.48 (br, 4H, O(CH_2CH_2)$_2$), 2.31 (s, 9H, CH_3 of Tp^{Me2}), 2.13 (s, 11H, CH_3 of Tp^{Me2} and CH_2Ph), 1.21 (br, 4H, O(CH_2CH_2)$_2$).

Synthesis of (Tp^{Me2})CpYC≡CPh(THF) (2). To a 15 mL THF solution of **1** (0.307 g, 0.5 mmol) was added phenylacetylene (0.051 g, 0.5 mmol) dropwise. After stirring overnight at room temperature, the solution was concentrated to ca. 5 mL under reduced pressure. Diffusion of *n*-hexane to the solution gave colorless crystals of **2**. Yield: 0.253 g (81%). Anal. Calcd for $C_{32}H_{40}BN_6OY$ (624.42): C, 61.55; H, 6.46; N, 13.46. Found: C, 61.72; H, 6.38; N, 13.61. ^{1}H NMR: δ 7.73−7.74 (m, 2H, C_6H_5), 7.18−7.20 (m, 2H, C_6H_5), 7.02−7.06 (m, 1H, C_6H_5), 6.61 (s, 5H, C_5H_5), 5.59 (br, 3H, 4H-Tp^{Me2}), 3.57 (br, 4H, O(CH_2CH_2)$_2$), 2.74 (br, 9H, CH_3 of Tp^{Me2}), 2.21 (s, 9H, CH_3 of Tp^{Me2}), 1.30 (br, 4H, O(CH_2CH_2)$_2$).

Synthesis of (Tp^{Me2})CpY[(^{i}PrN)$_2$C(CH$_2$Ph)] (3a). To a 15 mL THF solution of **1** (0.307 g, 0.5 mmol) was added ^{i}PrN=C=^{i}Pr (0.051 g, 0.5 mmol) at room temperature. The yellow-green mixture was stirred for 12 h. After removing the solvent under reduced pressure, the residue was dissolved in 8 mL of toluene. The solution was layered by *n*-hexane to afford **3a** as colorless crystals. Yield: 0.234 g (70%). Anal. Calcd for $C_{34}H_{48}BN_8Y$ (668.52): C, 61.09; H, 7.24; N, 16.76. Found: C, 60.82; H, 7.35; N, 16.94. ^{1}H NMR: δ 7.44−7.46 (m, 2H, C_6H_5), 7.23−7.27 (m, 2H, C_6H_5), 7.11−7.13 (m, 1H, C_6H_5), 6.45 (s, 5H, C_5H_5), 5.68 (s, 2H, 4H-Tp^{Me2}), 5.60 (s, 1H, 4H-Tp^{Me2}), 3.69−3.75 (m, 4H, $CH(CH_3)_2$ and CH_2Ph), 2.53 (s, 6H, CH_3 of Tp^{Me2}), 2.24 (s, 3H, CH_3 of Tp^{Me2}), 2.16 (s, 6H, CH_3 of Tp^{Me2}), 2.00 (s, 3H, CH_3 of Tp^{Me2}), 1.22 (d, 6H, CH(CH_3)$_2$, J = 6.4 Hz), 0.96 (d, 6H, CH(CH_3)$_2$, J = 6.4 Hz).

Synthesis of (Tp^{Me2})CpY[(CyN)$_2$C(CH$_2$Ph)] (3b). Following the procedure described above for **3a**, the reaction of **1** (0.307 g, 0.5 mmol) with *N*,*N*′-dicyclohexylcarbodiimide (DCC; 0.103 g, 0.5 mmol) in 15 mL of THF at room temperature gave colorless crystals of **3b**.

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Table 2. Crystal and Data Collection Parameters of Complexes 3c, 4, 5, and 6

	3c	4·1/2C_6H_{14}	5	6
formula	$C_{52}H_{68}BN_8Y$	$C_{37}H_{46}BN_7SY$	$C_{34}H_{39}BN_7OY$	$C_{28}H_{34}BN_6S_2Y$
mw	904.86	720.59	661.44	618.45
cryst color	colorless	pale yellow	colorless	pale red
cryst dimens (mm)	0.17 × 0.10 × 0.08	0.25 × 0.10 × 0.08	0.15 × 0.20 × 0.25	0.20 × 0.15 × 0.04
cryst syst	hexagonal	triclinic	monoclinic	monoclinic
space group	$R\bar{3}$	$P\bar{1}$	$P2(1)/n$	$P2(1)/c$
unit cell dimensions				
a (Å)	49.363(19)	10.703(4)	15.777(6)	17.901(7)
b (Å)	49.363(13)	12.479(5)	10.716(4)	8.446(3)
c (Å)	10.871(4)	16.059(6)	19.971(7)	20.014(7)
α (deg)	90.00	72.488(4)	90.00	90.00
β (deg)	90.00	74.979(4)	104.750(5)	98.456(5)
γ (deg)	120.00	66.018(4)	90.00	90.00
V (Å^3)	22942(13)	1845.7(12)	3265(2)	2993.3(19)
Z	18	2	4	4
D_{calcd} (g cm^{-3})	1.179	1.297	1.346	1.372
μ (mm^{-1})	1.185	1.672	1.824	2.116
F (000)	8640	754	1376	1280
radiation (λ = 0.710730 Å)	Mo Kα	Mo Kα	Mo Kα	Mo Kα
temperature (K)	293(2)	293(2)	293(2)	293(2)
scan type	ω-2θ	ω-2θ	ω-2θ	ω-2θ
θ range (deg)	1.43−25.01	1.35−25.01	1.48−25.01	1.15−25.51
h, k, l range	$-58 \le h \le 50$	$-12 \le h \le 11$	$-18 \le h \le 18$	$-21 \le h \le 18$
	$-50 \le k \le 58$	$-14 \le k \le 10$	$-12 \le k \le 12$	$-10 \le k \le 9$
	$-12 \le l \le 12$	$-19 \le l \le 1$	$-12 \le l \le 23$	$-24 \le l \le 24$
no. of reflns measured	37830	9149	13153	12599
no. of unique reflns	8975 [R(int) = 0.1486]	6388 [R(int) = 0.1026]	5728 [R(int) = 0.0603]	5565 [R(int) = 0.0587]
completeness to θ	100.0% (θ = 25.01)	98.2% (θ = 25.01)	99.6% (θ = 25.01)	99.7% (θ = 25.51)
max. and min. transmission	0.9112 and 0.8239	0.8779 and 0.6799	0.7715 and 0.6584	0.9202 and 0.6770
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	8975/0/576	6388/4/427	5728/13/389	5565/0/352
Goodness-of-fit on F^2	0.958	0.977	0.936	0.856
final R indices [$I > 2\sigma$ (I)]	R_1 = 0.0592	R_1 = 0.0542	R_1= 0.0530	R_1 = 0.0377
	wR_2 = 0.1376	wR_2 = 0.1173	wR_2 = 0.1256	wR_2 = 0.0595
R indices (all data)	R_1 = 0.1275	R_1 = 0.0825	R_1 = 0.0936	R_1 = 0.0853
	wR_2 = 0.1601	wR_2 = 0.1233	wR_2 = 0.1420	wR_2 = 0.0703
largest diff. peak and hole (e Å^{-3})	0.730 and −0.517	0.947 and −0.542	0.664 and −0.607	0.369 and −0.416

Yield: 0.232 g (62%). Anal. Calcd for $C_{40}H_{56}BN_8Y$ (748.65): C, 64.17; H, 7.54; N, 14.97. Found: C, 63.97; H, 7.67; N, 15.26. ^{1}H NMR: δ 7.50−7.52 (m, 2H, C_6H_5), 7.22−7.26 (m, 2H, C_6H_5), 7.10−7.12 (m, 1H, C_6H_5), 6.49 (s, 5H, C_5H_5), 5.72 (s, 2H, 4H-Tp^{Me2}), 5.62 (s, 1H, 4H-Tp^{Me2}), 3.76 (s, 2H, CH_2Ph), 3.29−3.37 (m, 2H, $CH(CH_2)_5$), 2.62 (s, 6H, CH_3 of Tp^{Me2}), 2.30 (s, 3H, CH_3 of Tp^{Me2}), 2.16 (s, 6H, CH_3 of Tp^{Me2}), 1.98 (s, 3H, CH_3 of Tp^{Me2}), 1.10−1.82 (m, 20H, $CH(CH_2)_5$).

Synthesis of (Tp^{Me2})CpY[(2,6-^{i}Pr−C_6H_3N)$_2$C(CH_2Ph)] (3c). Following the procedure described above for **3a**, the reaction of **1** (0.307 g, 0.5 mmol) with *N*,*N*′-2,6-diisopropylphenylcarbodiimide (BPC; 0.182 g, 0.5 mmol) in 15 mL of THF at 55 °C for a week afforded colorless crystals of **3c**. Yield: 0.276 g (61%). Anal. Calcd for $C_{52}H_{68}BN_8Y$ (904.86): C, 69.02; H, 7.57; N, 12.38. Found: C, 68.83; H, 7.50; N, 12.61. ^{1}H NMR: δ 7.32−7.34 (m, 2H, C_6H_5 or C_6H_3), 7.20−7.25 (m, 2H, C_6H_5 or C_6H_3), 7.05−7.07 (m, 3H, C_6H_5 or C_6H_3), 6.86−6.88 (m, 2H, C_6H_5 or C_6H_3), 6.66−6.68 (m, 2H, C_6H_5 or C_6H_3), 5.99 (s, 5H, C_5H_5), 5.60 (s, 1H, 4H-Tp^{Me2}), 5.51 (s, 2H, 4H-Tp^{Me2}), 4.08 (s, 2H, CH_2Ph), 3.62−3.69 (m, 4H, $CH(CH_3)_2$), 2.43 (s, 3H, CH_3 of Tp^{Me2}), 2.12 (s, 6H, CH_3 of Tp^{Me2}), 1.94 (s, 3H, CH_3 of Tp^{Me2}), 1.77 (s, 6H, CH_3 of Tp^{Me2}), 1.55 (d, 6H, $CH(CH_3)_2$, J = 6.4 Hz), 1.24 (d, 12H, $CH(CH_3)_2$, J = 6.8 Hz), 0.74 (d, 6H, $CH(CH_3)_2$, J = 6.4 Hz).

Synthesis of (Tp^{Me2})CpY[SC(CH_2Ph)NPh] (4). To a 15 mL THF solution of **1** (0.307 g, 0.5 mmol) was added phenyl isothiocyanate (0.068 g, 0.5 mmol) dropwise at room temperature. The pale red-yellow mixture was stirred overnight at room temperature. The mixture was evaporated to dryness under reduced pressure. Then, to the residue was added 8 mL of toluene; the toluene solution of **4** was layered with *n*-hexane to afford colorless crystals of **4**·0.5C_6H_{14}. Yield: 0.227 g (63%). Anal. Calcd for $C_{37}H_{46}BN_7SY$ (720.59): C, 61.67; H, 6.43; N, 13.61. Found: C, 61.94; H, 6.25; N, 13.90. ^{1}H NMR: δ 7.50−7.51 (m, 2H, C_6H_5), 7.19−7.23 (m, 2H, C_6H_5), 7.09−7.12 (m, 1H, C_6H_5), 6.98−6.99 (m, 4H, C_6H_5), 6.89−6.94 (m, 1H, C_6H_5), 6.21 (s, 5H, C_5H_5), 5.53 (s, 1H, 4H-Tp^{Me2}), 5.50 (s, 1H, 4H-Tp^{Me2}), 5.49 (s, 1H, 4H-Tp^{Me2}), 3.98 (d, 1H, CH_2Ph, J = 13.6 Hz), 3.90 (d, 1H, CH_2Ph, J = 13.6 Hz), 2.47 (s, 3H, CH_3 of Tp^{Me2}), 2.23 (s, 3H, CH_3 of Tp^{Me2}), 2.18 (s, 3H, CH_3 of Tp^{Me2}), 2.15 (s, 3H, CH_3 of Tp^{Me2}), 1.97 (s, 3H, CH_3 of Tp^{Me2}), 1.56 (s, 3H, CH_3 of Tp^{Me2}).

Synthesis of (Tp^{Me2})CpY[OC(CH_2Ph)NPh] (5). To a 15 mL THF solution of **1** (0.307 g, 0.5 mmol) was added phenyl isocyanate (0.060 g, 0.5 mmol) dropwise at −35 °C. The colorless mixture was allowed to slowly warm to room temperature and stirred overnight. The volatile was removed under reduced pressure, and the residue was solvated in 6 mL of toluene. Diffusing of *n*-hexane to the solution gave the desired product **5** as colorless crystals. Yield: 0.132 g (40%). Anal. Calcd for $C_{34}H_{39}BN_7OY$ (661.44): C, 61.74; H, 5.94; N, 14.82.

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Table 3. Crystal and Data Collection Parameters of Complexes 7a, 7b, 9, and 10

	7a·1/2C_6H_{14}	7b·THF	9	10
formula	$C_{38}H_{53}BN_8Y$	$C_{45}H_{62}BN_8OY$	$C_{35}H_{37}BN_7SY$	$C_{33}H_{45}BN_7OY$
mw	721.60	830.75	687.50	655.48
cryst color	coloeless	coloeless	colorless	colorless
cryst dimens (mm)	0.25 × 0.20 × 0.10	0.15 × 0.12 × 0.08	0.14 × 0.13 × 0.11	0.16 × 0.12 × 0.10
cryst syst	triclinic	monoclinic	orthorhombic	triclinic
space group	$P\bar{1}$	$P2(1)/n$	$Pna2(1)$	$P\bar{1}$
unit cell dimensions				
a (Å)	9.769(3)	10.981(4)	21.913(7)	10.957(5)
b (Å)	10.814(4)	23.551(8)	8.719(3)	12.032(6)
c (Å)	20.836(7)	17.615(6)	18.341(6)	13.200(7)
α (deg)	94.686(5)	90.00	90.00	93.843(7)
β (deg)	98.712(5)	99.677(5)	90.00	94.354(7)
γ (deg)	116.286(4)	90.00	90.00	106.606(7)
V (Å^3)	1923.1(11)	4491(3)	3504.2(18)	1655.7(14)
Z	2	4	4	2
D_{calcd} (g cm^{-3})	1.246	1.229	1.303	1.315
μ (mm^{-1})	1.553	1.341	1.758	1.798
F (000)	762	1760	1424	688
Radiation (λ = 0.710730 Å)	Mo Kα	Mo Kα	Mo Kα	Mo Kα
temperature (K)	293(2)	293(2)	293(2)	293(2)
scan type	ω-2θ	ω-2θ	ω-2θ	ω-2θ
θ range (deg)	2.01−25.00	1.46−25.01	1.86−25.10	1.55−25.50
h, k, l range	$-11 \le h \le 11$	$-12 \le h \le 13$	$-26 \le h \le 25$	$-13 \le h \le 13$
	$12 \le k \le 10$	$28 \le k \le 26$	$10 \le k \le 10$	$14 \le k \le 13$
	$-18 \le l \le 24$	$-20 \le l \le 13$	$-10 \le l \le 21$	$15 \le l \le 15$
no. of reflns measured	7979	18419	14065	7159
no. of unique reflns	6620 [R(int) = 0.0379]	7880 [R(int) = 0.0625]	4973 [R(int) = 0.0592]	5986 [R(int) = 0.0485]
completeness to θ	97.8% (25.00)	99.7%(25.01)	100.0%(25.01)	97.1% (25.50)
max. and min. transmission	0.8602 and 0.6975	0.9003 and 0.8242	0.8301 and 0.7909	0.8407 and 0.7618
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	6620/2/436	7880/7/483	4973/2/409	5986/0/398
goodness-of-fit on F^2	0.939	0.943	0.919	1.021
final R indices [$I > 2\sigma$ (I)]	R_1 = 0.0526	R_1 = 0.0552	R_1 = 0.0413	R_1 = 0.0695
	wR_2 = 0.1345	wR_2 = 0.1540	wR_2 = 0.0982	wR_2 = 0.2035
R indices (all data)	R_1 = 0.0857	R_1 = 0.0994	R_1 = 0.0640	R_1 = 0.0999
	wR_2 = 0.1531	wR_2 = 0.1684	wR_2 = 0.1150	wR_2 = 0.2187
largest diff. peak and hole (e Å^{-3})	0.449 and −0.364	0.727 and −0.705	0.475 and −0.358	1.616 and −0.557

Found: C, 62.06; H, 6.08; N, 14.57. ^{1}H NMR: δ 7.57−7.59 (m, 2H, C_6H_5), 7.25−7.29 (m, 2H, C_6H_5), 7.09−7.13 (m, 3H, C_6H_5), 6.94−7.01 (m, 3H, C_6H_5), 6.21 (s, 5H, C_5H_5), 5.52 (s, 3H, 4H-Tp^{Me2}), 3.61 (s, 2H, CH_2Ph), 2.12 (s, 18H, CH_3 of Tp^{Me2}).

Synthesis of (Tp^{Me2})CpY[S$_2$C(CH$_2$Ph)] (6). To a 15 mL THF solution of **1** (0.307 g, 0.5 mmol) was added dropwise CS_2 (0.046 g, 0.6 mmol) at −35 °C. After stirring for 20 min at −35 °C, the red solution was concentrated to ca. 6 mL. The concentrated THF solution was diffused by *n*-hexane to afford pale-red colorless crystals of **6**. Yield: 0.176 g (57%). Anal. Calcd for $C_{28}H_{34}BN_6S_2Y$ (618.45): C, 54.38; H, 5.54; N, 13.59. Found: C, 54.62; H, 5.67; N, 13.34. ^{1}H NMR: δ 7.60−7.62 (m, 2H, C_6H_5), 7.21−7.25 (m, 2H, C_6H_5), 7.10−7.14 (m, 1H, C_6H_5), 6.04 (s, 5H, C_5H_5), 5.44 (s, 3H, 4H-Tp^{Me2}), 4.49 (s, 2H, CH_2Ph), 2.20 (s, 9H, CH_3 of Tp^{Me2}), 2.08 (s, 9H, CH_3 of Tp^{Me2}).

Synthesis of (Tp^{Me2})CpY[(^{i}PrN)$_2$C(C≡CPh)] (7a). To a 15 mL THF solution of **2** (0.312 g, 0.5 mmol) was added N,N′-diisopropylcarbodiimide (DIC) (0.051 g, 0.5 mmol) at room temperature. The mixture was stirred for 12 h at room temperature. After removing the volatile, the residue was dissolved in 6 mL of toluene. The toluene solution was diffused by *n*-hexane to give colorless crystals **7a**·0.5C_6H_{14}. Yield: 0.242 g (67%). Anal. Calcd for $C_{38}H_{53}BN_8Y$ (721.60): C, 63.25; H, 7.40; N, 15.53. Found: C, 62.86; H, 7.48; N, 15.62. ^{1}H NMR: δ 7.46−7.49 (m, 2H, C_6H_5), 6.98−7.00 (m, 3H, C_6H_5), 6.45 (s, 5H, C_5H_5), 5.68 (s, 2H, 4H-Tp^{Me2}), 5.53 (s, 1H, 4H-Tp^{Me2}), 4.31−4.41 (m, 2H, $CH(CH_3)_2$), 2.55 (s, 6H, CH_3 of Tp^{Me2}), 2.40 (s, 3H, CH_3 of Tp^{Me2}), 2.16 (s, 6H, CH_3 of Tp^{Me2}), 1.98 (s, 3H, CH_3 of Tp^{Me2}), 1.63 (d, 6H, $CH(CH_3)_2$, J = 6.4 Hz), 1.13 (d, 6H, $CH(CH_3)_2$, J = 6.4 Hz).

Synthesis of (Tp^{Me2})CpY[(CyN)$_2$C(C≡CPh)] (7b). Following the procedure described above for **7a**, the reaction of **2** (0.312 g, 0.5 mmol) with N,N′-dicyclohexancarbodiimide (DCC; 0.103 g, 0.5 mmol) in 15 mL of THF at room temperature gave colorless crystals of **7b**·THF. Yield: 0.291 g (70%). Anal. Calcd for $C_{45}H_{62}BN_8OY$ (830.75): C, 65.06; H, 7.52; N, 13.49. Found: C, 64.73; H, 7.58; N, 13.66. ^{1}H NMR: δ 7.55−7.57 (m, 2H, C_6H_5), 7.00−7.02 (m, 3H, C_6H_5), 6.48 (s, 5H, C_5H_5), 5.72 (s, 2H, 4H-Tp^{Me2}), 5.52 (s, 1H, 4H-Tp^{Me2}), 3.93−4.03 (m, 2H, $CH(CH_2)_5$), 2.62 (s, 6H, CH_3 of Tp^{Me2}), 2.43 (s, 3H, CH_3 of Tp^{Me2}), 2.17 (s, 6H, CH_3 of Tp^{Me2}), 1.98 (s, 3H, CH_3 of Tp^{Me2}), 1.19−1.98 (m, 20H, $CH(CH_2)_5$).

Synthesis of *N,N′*-Disubstituted Propiolamidines RN=C(C≡CPh)(NHR) (R = ^{i}Pr (8a), Cy(8b)). In the glovebox, a 3 mL THF or 3 mL toluene solution of phenylacetylene (0.211 g, 2.07 mmol) was added to a 2 mL THF or 2 mL toluene solution of complex **1** (0.037 g, 0.06 mmol). Then, ^{i}PrN=C=N^{i}Pr (0.255 g, 2.01 mmol) was added to the above reaction mixture. The Schlenk tube was taken out, and the mixture was stirred at 80 °C for 3 h (THF) or at 110 °C for 2 h (toluene). After the solvent was removed under reduced pressure, the

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residue was extracted with hexane and filtered to give a clean solution. After removing the solvent under vacuum conditions, the residue was recrystallized in *n*-hexane to give the desired solid product **8a**. Yield: 0.450 g (98%). ^{1}H NMR: δ 7.38−7.40 (m, 2H, C_6H_5), 6.94−6.98 (m, 3H, C_6H_5), 4.24−4.27 (m, 2H, $CH(CH_3)_2$), 3.77 (brs, 1H, NH), 1.40 (d, 6H, J = 5.2 Hz, $CH(CH_3)_2$), 0.99 (d, 6H, J = 6.0 Hz, $CH(CH_3)_2$).

Following the procedure described above for **8a**, the reaction of phenylacetylene (0.211 g, 2.07 mmol) with DCC (0.415 g, 2.01 mmol) under complex **1** (0.037 g, 0.06 mmol) as a catalyst in 5 mL of THF or 5 mL of toluene afforded the desired product **8b**. Yield: 0.595 g (96%). ^{1}H NMR: δ 7.42−7.44 (m, 2H, C_6H_5), 6.97−6.98 (m, 3H, C_6H_5), 3.98 (brs, 2H, $CH(CH_2)_5$), 3.94 (brs, 1H, NH), 0.94−2.05 (m, 20H, $CH(CH_2)_5$)

Synthesis of (Tp^{Me2})CpY[SC(C≡CPh)NPh] (9). To a 15 mL THF solution of **2** (0.312 g, 0.5 mmol) was added phenyl isothiocyanate (0.068 g, 0.5 mmol) dropwise at room temperature. The mixture was stirred for 12 h at room temperature. After removing the volatile, the residue was dissolved in toluene (6 mL). The solution of toluene was diffused by *n*-hexane to give the colorless crystals **9**. Yield: 0.306 g (89%). Anal. Calcd for $C_{35}H_{37}BN_7SY$ (687.50): C, 61.15; H, 5.42; N, 14.26. Found: C, 60.88; H, 5.55; N, 14.53. ^{1}H NMR: δ 7.34−7.36 (m, 2H, C_6H_5), 7.21−7.23 (m, 2H, C_6H_5), 7.05−7.08 (m, 2H, C_6H_5), 6.97−7.00 (m, 1H, C_6H_5), 6.90−6.88 (m, 3H, C_6H_5), 6.30 (s, 5H, C_5H_5), 5.60 (s, 1H, 4H-Tp^{Me2}), 5.52 (s, 1H, 4H-Tp^{Me2}), 5.42 (s, 1H, 4H-Tp^{Me2}), 2.68 (s, 3H, CH_3 of Tp^{Me2}), 2.27 (s, 3H, CH_3 of Tp^{Me2}), 2.19 (s, 3H, CH_3 of Tp^{Me2}), 2.17 (s, 3H, CH_3 of Tp^{Me2}), 1.98 (s, 3H, CH_3 of Tp^{Me2}), 1.80 (s, 3H, CH_3 of Tp^{Me2}).

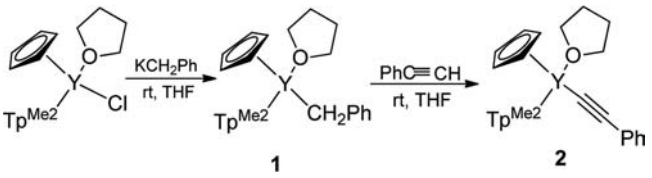
Synthesis of (Tp^{Me2})CpY(NHC$_6$H$_4$CH$_2$CH═CH$_2$-*o*)(THF) (10). To a 15 mL THF solution of **1** (0.307 g, 0.5 mmol) in a sealed tube was added *o*-allylaniline (0.067 g, 0.5 mmol) at room temperature. After being stirred at 85 °C overnight, the volatiles were removed under vacuum conditions; the residue was dissolved in 6 mL of toluene. The toluene solution of complex **10** was evaporated slowly in a glovebox to afford colorless crystals **10**. Yield: 0.275 g (84%). Anal. Calcd for $C_{33}H_{45}BN_7OY$ (655.48): C, 60.47; H, 6.92; N, 14.96. Found: C, 60.31; H, 6.81; N, 15.14. ^{1}H NMR: δ 7.01−7.03 (m, 1H, C_6H_5), 6.69−6.72 (m, 1H, C_6H_5), 6.39−6.43 (m, 1H, C_6H_5), 6.35 (s, 5H, C_5H_5), 6.01−6.04 (m, 1H, C_6H_5), 5.74 (br, 1H, NH), 5.57(br, 3H, 4H-Tp^{Me2}), 5.11(d, 1H, $CH_2C_2H_3$, J = 17.6 Hz), 5.05 (d, 1H, $CH_2C_2H_3$, J = 10 Hz), 4.93 (s, 1H, $CH_2C_2H_3$), 3.56 (s, 4H, $O(CH_2CH_2)_2$), 3.34(d, 2H, $CH_2C_2H_3$, J = 5.6 Hz), 2.13−2.15 (dbr, 18H, CH_3 of Tp^{Me2}), 1.47 (s, 4H, $O(CH_2CH_2)_2$).

X-Ray Data Collection, Structure Determination and Refinement. Suitable single crystals of all complexes **1**−**7**, **9**, and **10** were sealed under argon in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption with SADABS program.[12] The structures were solved by the direct method using the SHELXL-97 program.[13] All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program. A summary of the crystallographic data and selected experimental information is given in Tables 1−3.

RESULTS AND DISCUSSION

Synthesis and Characterizations of Mixed Tp^{Me2}/Cp Yttrium Alkyl and Alkynyl Complexes (Tp^{Me2})CpYCH$_2$Ph-(THF) (1) and (Tp^{Me2})CpYC≡CPh(THF) (2). In contrast to the reactions of (Tp^{Me2})$_2$LnCl (Ln = Sm, Nd) with KCH_2SiMe_3 and $KC_6H_4NMe_2$, wherein only the metal-reduced or ligand-degraded product was often obtained,[6] treatment of (Tp^{Me2})CpYCl(THF) with 1 equiv of KCH_2Ph in THF at room temperature afforded the expected yttrium benzyl complex (Tp^{Me2})CpYCH$_2$Ph(THF) (**1**) in 83% isolated yield

Scheme 1



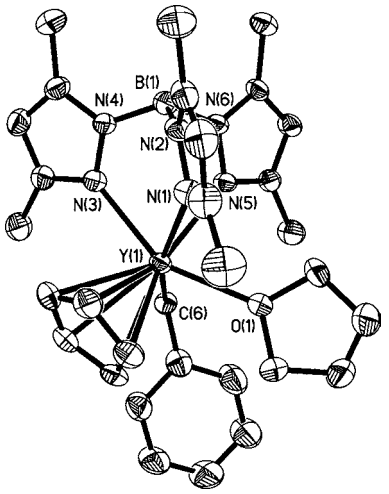


Figure 1. ORTEP diagram of (Tp^{Me2})CpYCH$_2$Ph(THF) (**1**) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−C6 2.528(3), Y1−O1 2.422(3), Y1−N3 2.462(3), Y1−N5 2.524(3), Y1−N1 2.553(4), C6−C7 1.492(6), Y1−C6−C7 123.1(3).

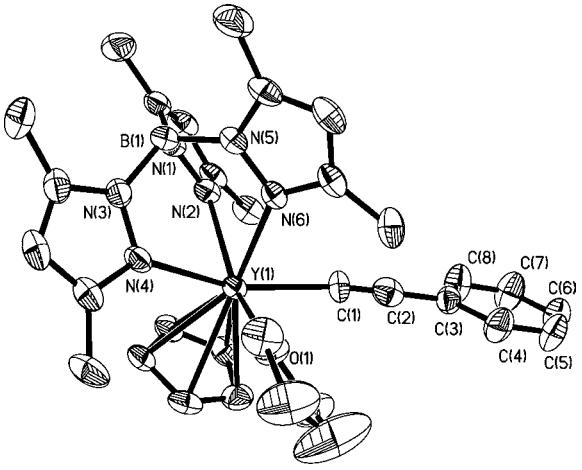


Figure 2. ORTEP diagram of (Tp^{Me2})CpYC≡CPh(THF) (**2**) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−C1 2.419(4), Y1−O1 2.399(3), Y1−N2 2.455(3), Y1−N4 2.508(3), Y1−N6 2.497(3), C1−C2 1.164(6), Y1−C1−C2 173.3(4).

(Scheme 1). Complex **1** is a suitable precursor for the synthesis of mixed Tp^{Me2}/Cp yttrium derivatives. For example, **1** reacted with 1 equiv of PhC≡CH at room temperature to give (Tp^{Me2})CpYC≡CPh(THF) (**2**) in 81% isolated yield.

Complexes **1** and **2** are air- and moisture-sensitive and readily soluble in THF and toluene but slightly soluble in hexane. They are characterized by elemental analysis and ^{1}H NMR spectroscopy, which are in good agreement with the proposed structures. In the ^{1}H NMR spectrum of **1**, three

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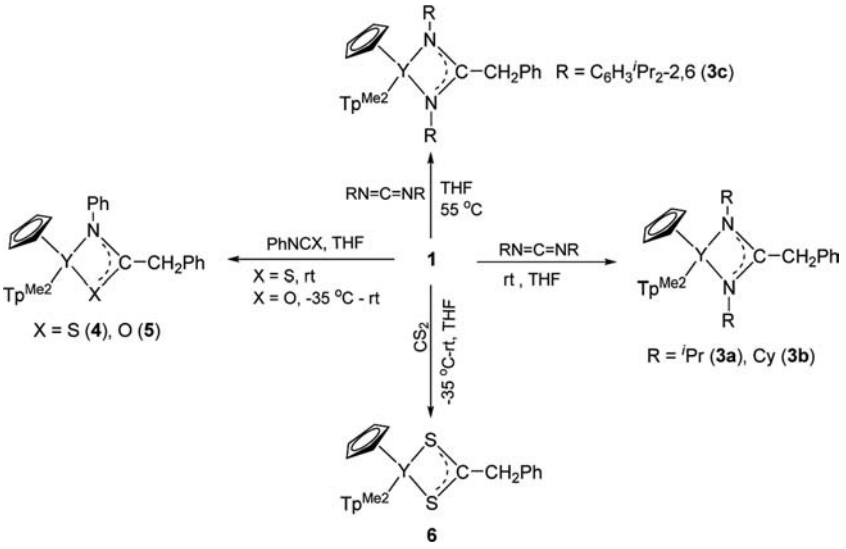
Scheme 2



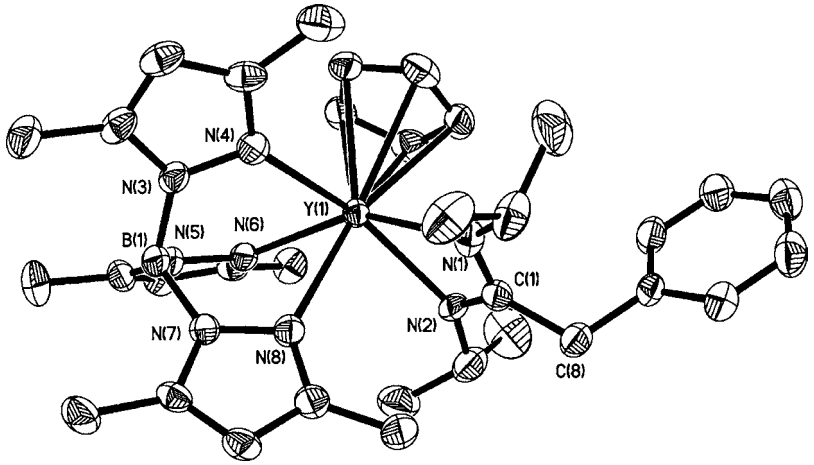


Figure 3. ORTEP diagram of **3a** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−N1 2.385(4), Y1−N2 2.387(3), Y1−C1 2.818(4), C1−C8 1.527(6), N1−C1 1.347(6), N2−C1 1.325(6), N1−Y1−N2 56.4(1), Y1−N1−C1 93.9(3), Y1−N2−C1 94.4(3), N2−C1−N1 115.2(4), N2−C1−C8 123.9(4), N1−C1−C8 120.8(4), Y1−C1−C8 178.5(4).

single peaks at 6.34, 5.60, 2.31, and 2.13 ppm are attributed to *H*-Cp, 4-*H*-Tp^{Me2}, 3-*Me*-Tp^{Me2}, and 5-*Me*-Tp^{Me2}, respectively, and there is a singlet for the Cp ring proton at 6.34 ppm and three multiple peaks at 7.38−6.92 ppm that are attributed to phenyl ring proton of the benzyl group. The CH_2 peak of the benzyl group is buried in the peak of 5-*Me*-Tp^{Me2} at 2.13 ppm. The similar peaks of ^{1}H NMR spectra of **2** were observed without the CH_2 peak of **1**. The solid-state structures of **1** and **2** were further confirmed by single-crystal X-ray diffraction analysis.

The molecular structures of **1** and **2**, including their selected bond lengths and angles, are compiled in Figures 1 and 2, respectively. The X-ray structural analysis results show that **1** and **2** are solvated monomers. In **1**, the yttrium atom is bonded to a κ^3-Tp^{Me2} ligand, an η^5-Cp ring, an η^1-benzyl group, and one THF molecule to form distorted facial-octahedral geometry, with the Cp, η^1-benzyl, and THF ligands in between the clefts formed by the pyrazolyl groups. The bonding mode of the benzyl group to metal is similar to that observed in $(C_5Me_5)_2Sm(\eta^1\text{-}CH_2Ph)(THF)$[14a] but different from that observed in $[(Me_3Si)_2NC(NCy)_2]Ln(\eta^3\text{-}CH_2Ph)$ (Ln = Er, Y).[14b] Considering the difference in metal ionic radius, the Y−C6 distance (2.528(3) Å) is slightly longer than the corresponding value found in $(C_5Me_5)_2Sm(\eta^1\text{-}CH_2C_6H_5)$-(THF) (2.528(8) Å), possibly due to the larger steric hindrance around the central metal in **1**. Consistent with this, the C7−C6−Y1 angle (123.1(3)°) is also larger than the corresponding value of $(C_5Me_5)_2Sm(\eta^1\text{-}CH_2Ph)(THF)$ (111.2 (5)°).

The overall structure of **2** is similar to that of **1**, except the replacement of $PhCH_2$ by the PhC≡C group. All bond parameters of the $(Tp^{Me2})CpY$ moiety in **2** are in the normal range. The Y1−C1 distance (2.419(4) Å) is an ideal Y−C(sp) distance and comparable to that observed in $[Me_2Si(NCMe_3)$-$(OCMe_3)]_2YC{\equiv}CPh(THF)$ (Y1−C1 2.448(4) Å).[15] The C1−C2 distance is 1.164(6) Å, in the range of the C≡C triple bond (1.10−1.23 Å),[16] and similar to that of $[\{(Tp^{Me2})$-$Y(\mu\text{-}C{\equiv}CR)\}_2(\mu\text{-}RC_4R)]$ (C5−C6 1.206(5) Å; C7−C8 1.202(5) Å)[9e] and $(Tp^{Me2})_2SmC{\equiv}CPh$ (C1−C2 1.206(12) Å).[9f] The Y−C1−C2 angle is 173.3(4)°, slightly deviated from the linear geometry.

Reactions of 1 with RNCNR, PhNCO, PhNCS, and CS_2. The study of the reactivity of organolanthanide complexes with

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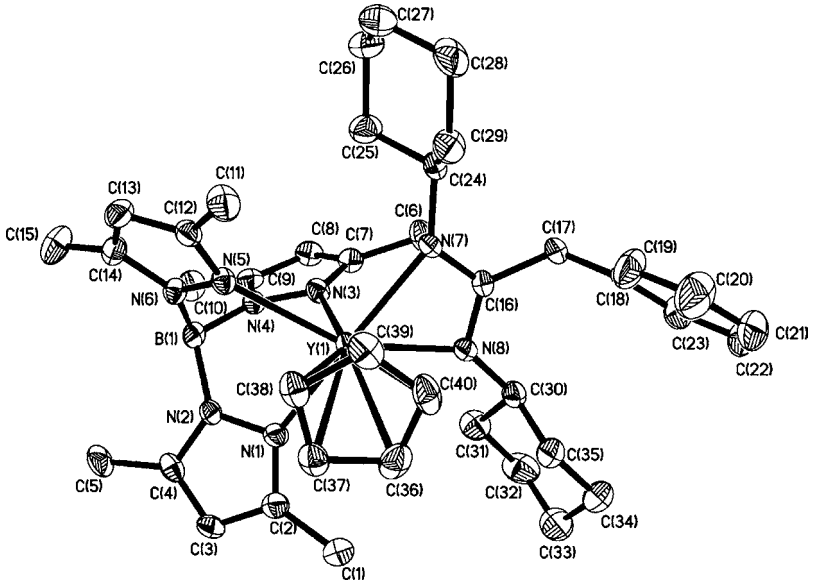

Figure 4. ORTEP diagram of **3b** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−N8 2.353(3), Y1−N7 2.359(3), Y1−C16 2.788(4), N7−C16 1.340(4), N8−C16 1.314(4), C16−C17 1.532(5), N8−Y1−N7 56.7(1), N8−C16−N7 114.8(3), N8−C16−C17 122.6(3), N7−C16−C17 122.6(3), Y1−C16−C17 179.8(3).

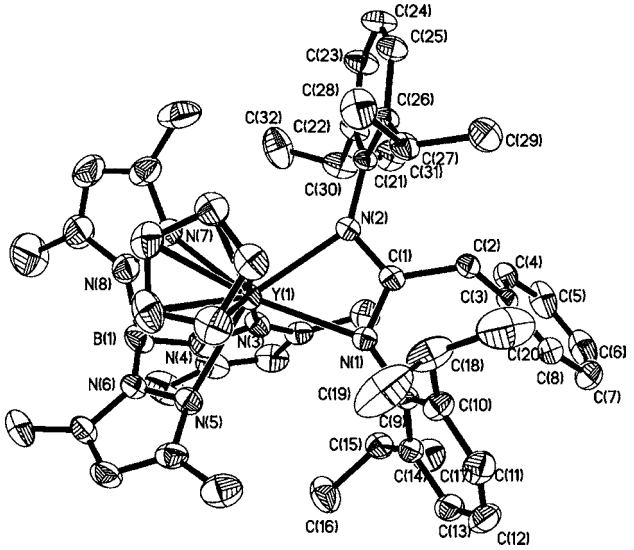

Figure 5. ORTEP diagram of **3c** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−N2 2.407(3), Y1−N1 2.460(3), Y1−C1 2.866(4), N1−C1 1.334(4), N2−C1 1.342(4), C1−C2 1.525(5), N2−Y1−N1 55.45(10), Y1−N1−C1 93.4(2), Y1−N2−C1 95.5(2), N1−C1−N2 115.6(3), N1−C1−C2 122.7(3), N2−C1−C2 121.7(3), Y1−C1−C2 177.7(3), C3−C2−C1 117.4(3).

unsaturated organic molecules is an important research field in organometallic chemistry, because this is the source for developing new catalytic reactions and catalysts. Due to the difficulty of the preparation of $Tp^{R,R'}$-supported lanthanide monoalkyl complexes, their reactivity toward unsaturated organic molecules was almost unexplored.[9f] To the best of our knowledge, only one example of a reaction of an organoactinide monoalky complex $(Tp^{Me2})_2UCH_2Ph$ with CO_2 or CS_2 has been recently reported.[17] With mixed Tp^{Me2}/Cp yttrium alkyl and alkynyl complexes **1** and **2** in hand, we next explored their reactivity toward some unsaturated substrates. As shown in Scheme 2, **1** can undergo

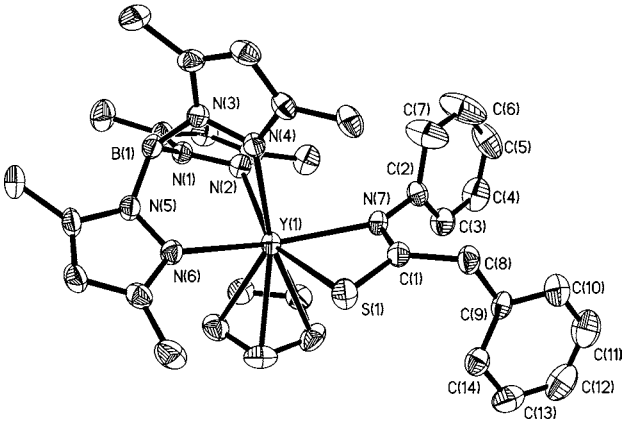

Figure 6. ORTEP diagram of complex **4** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−N7 2.433(3), Y1−S1 2.8109(16), Y1−C1 2.999(5), S1−C1 1.731(5), N7−C1 1.297(5), C1−C8 1.537(6), N7−Y1−S1 59.4(1), Y1−S1−C1 78.7(2), Y1−N7−C1 102.7(3), N7−C1−C8 123.8(4), N7−C1−S1 119.0(3), C8−C1−S1 117.3(4), Y1−C1−C8 175.2(3).

the Y−C σ-bond insertion with various unsaturated substrates. Treatment of **1** with 1 equiv of RN═C═NR (R = ^{i}Pr, Cy) in THF at room temperature afforded the monoinsertion products $(Tp^{Me2})CpY[(RN)_2CCH_2Ph]$ (R = ^{i}Pr(**3a**), Cy(**3b**)) in 70% and 62% yields, respectively, but for more bulky 2,6-$^i Pr_2C_6H_3N$═C═$NC_6H_3{}^iPr_2$-2,6, the reaction need to be carried out at elevated temperatures. With prolonged heating at 55 °C for a week, an isolated yield (61%) of $(Tp^{Me2})CpY[(RN)_2C(CH_2Ph)]$ (R = $C_6H_3{}^iPr_2$-2,6 (**3c**)) was obtained. This difference might be attributed to the large steric hindrance of the $C_6H_3{}^iPr_2$-2,6 substituent, preventing coordination of carbodiimide to the central metal ion, Y^{3+}.

Reaction of **1** with phenyl isothiocyanate (PhNCS) in THF at room temperature gave the thioamido complex $(Tp^{Me2})CpY[SC(CH_2Ph)NPh]$ (**4**) in 63% isolated yield, while **1**

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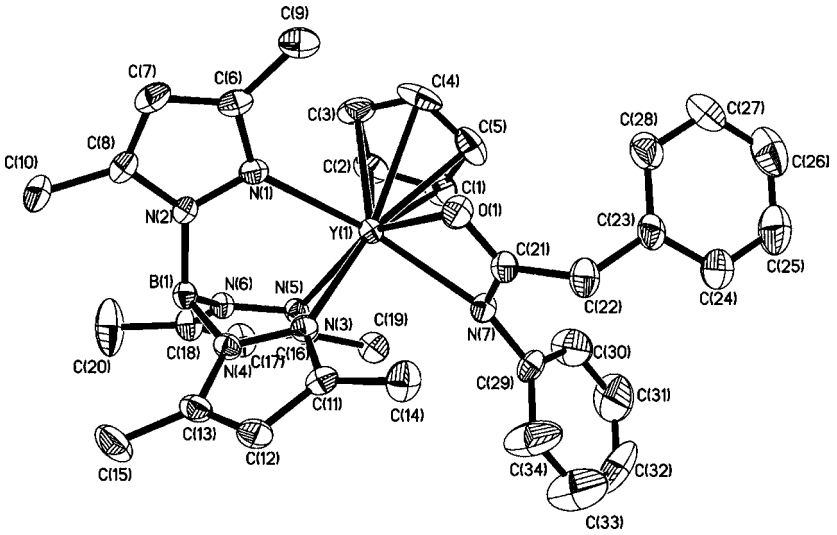


Figure 7. ORTEP diagram of complex **5** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−O1 2.285(3), Y1−N7 2.416(4), Y1−C21 2.735(5), N7−C21 1.299(6), O1−C21 1.276(6), C21−C22 1.526(7), O1−Y1−N7 56.0(1), Y1−O1−C21 96.2(3), Y1−N7−C21 89.6(3), O1−C21−N7 118.2(4), O1−C21−C22 117.5(4), N7−C21−C22 124.4(5), Y1−C21−O1 56.2(2), Y1−C21−N7 62.1(3), Y1−C21−C22 173.0(4).

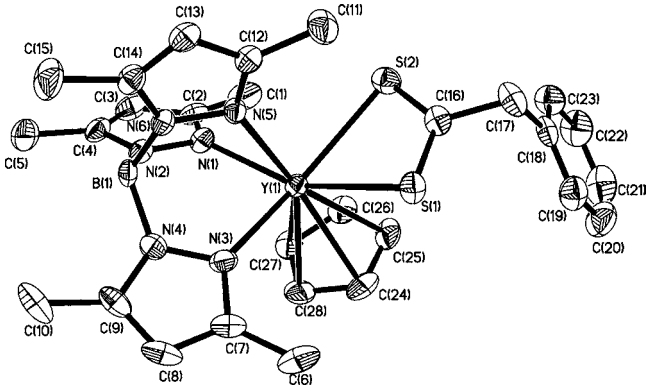
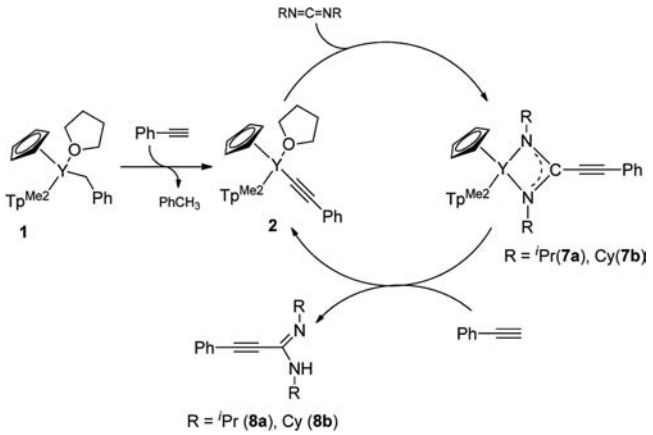


Figure 8. ORTEP diagram of complex **6** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−S1 2.831(1), Y1−S2 2.834(1), S1−C16 1.682(3), S2−C16 1.679(3), C16−C17 1.515(4), Y1−S1− C16 86.1(1), Y1−S2−C16 86.0(1), C17−C16−S2 118.3(3), C17−C16−S1 118.4(3), S2−C16−S1 123.3(2).

Scheme 3



reacted with PhNCO to afford the insertion product (Tp^{Me2})-CpY[OC(CH_2Ph)NPh] (**5**) in 40% isolated yield (Scheme 2).

In addition, **1** reacted with 1 equiv or a slight excess of CS_2 in THF for 20 min from −35 °C to room temperature to produce a pale-red complex (Tp^{Me2})CpY(S_2CCH_2Ph) (**6**) in 51% isolated yield.

All of these complexes were characterized by elemental analysis, ^{1}H NMR spectroscopy, and single-crystal X-ray analysis. The ^{1}H NMR spectra of these compounds displayed a different number of signals, in agreement with their solid-state structures. For example, the peak for 4H-Tp^{Me2} in ^{1}H NMR spectra of **3a** is separated into two single peaks at 5.68 and 5.60 ppm as a molar ratio of 2:1, and the peaks for 3 and 5-*Me*-Tp^{Me2} also split into four single peaks at 2.53, 2.24, 2.16, and 2.00 ppm in a 2:1:2:1 ratio. However, in ^{1}H NMR spectra of **4**, the single peak for 4H-Tp^{Me2} is split into three single peaks at 5.53 ppm, 5.50 ppm, and 5.49 ppm as a molar ratio of 1:1:1, and the peaks for 3- and 5-*Me*-Tp^{Me2} are separated into six single peaks at 2.47, 2.23, 2.18, 2.15, 1.97, and 1.56 ppm in a 1:1:1:1:1:1 ratio. Interestingly, in the ^{1}H NMR spectra of complex **5**, only a singlet peak at 2.12 ppm for 3- and 5-*Me*-Tp^{Me2} was observed, accompanied by one peak at 5.52 ppm for 4H-Tp^{Me2}.

The molecular structures and selected bond parameters of **3a**−**c** are given in Figures 3−5, respectively. The center metal, Y^{3+} in **3a**−**c** is bonded to one κ^3-Tp^{Me2}, one η^5-Cp group, and one chelating amidinate ligand. As expected, the amidinate group forms essentially a planar four-membered ring with the yttrium atom within experimental error. The bond angles around the center carbon atom (C1) in the planar four-membered rings are consistent with sp^2 hybridization. In **3a**, the two C−N bond distances of the amidinate group (C1−N1 and C1−N2, 1.347(6) and 1.325(6) Å) are approximately equivalent and significantly shorter than the C(sp^2)−N(sp^3) single bond distances (1.47−1.50 Å), indicating that the π electrons of the C═N double bond in the present structures are delocalized over the N ¨− C ¨− N unit.[18] Consistent with this observation, the Y−N1 and Y−N2 distances (2.385(4) and 2.387(3) Å) are intermediate between the values observed for a Y−N single bond distance and a Y−N donor bond distance[18] and are longer than the corresponding values found in

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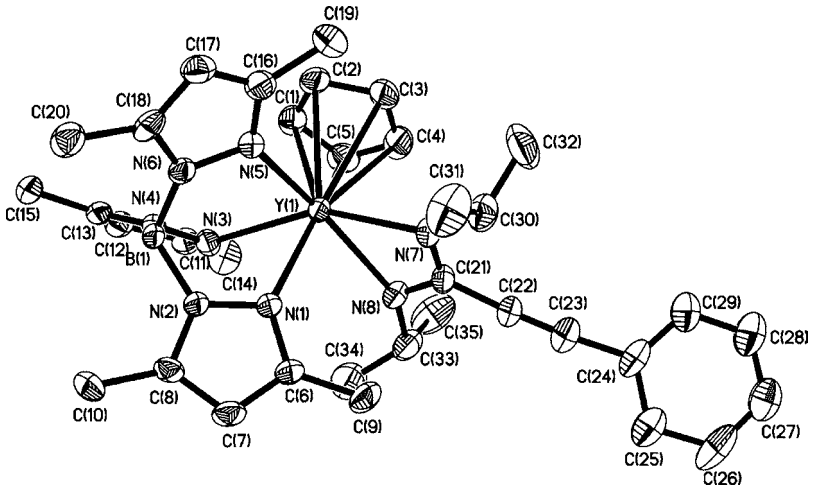

Figure 9. ORTEP diagram of complex **7a** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for complex **7a**. Y1−N8 2.374(4), Y1−N(7) 2.384(4), Y1−C21 2.774(5), N7−C21 1.319(6), N8−C21 1.310(6), C21−C22 1.447(6), C22−C23 1.190(7), N8−Y1−N7 56.4(2), Y1−N7−C21 92.5(3), Y1−N8−C21 93.2(3), N8−C21−N7 117.5(4), N8−C21−C22 120.5(5), N7−C21−C22 122.0(5), Y1−C21−C22 175.0(4), C23−C22−C21 176.6(6).

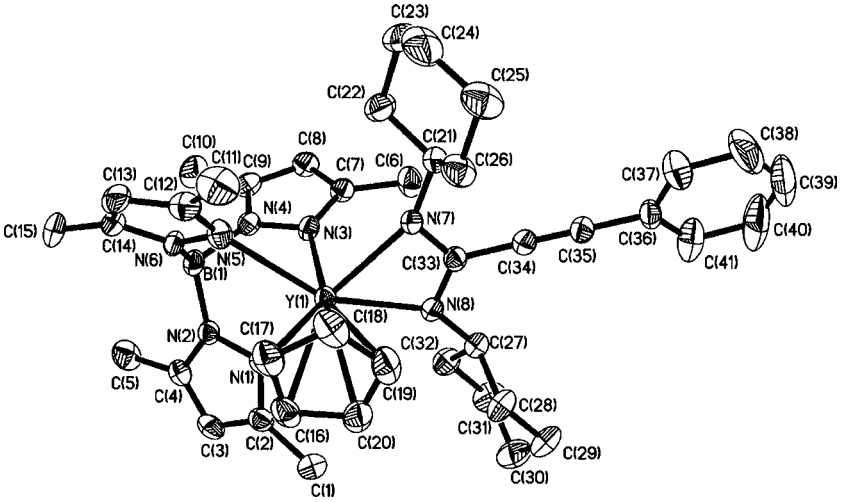

Figure 10. ORTEP diagram of complex **7b** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−N7 2.373(4), Y1−N8 2.390(4), Y1−C33 2.776(5), N7−C33 1.331(6), N8−C33 1.332(6), C33−C34 1.455(7), C34−C35 1.194(6), N7−Y1−N8 57.1(1), Y1−N7−C33 92.8(3), Y1−N8−C33 92.0(3), N7−C33−N8 117.4(4), N7−C33−C34 120.7(4), N8−C33−C34 121.8(4), Y1−C33−C34 172.5(3), C35−C34−C33 176.2(5).

$Cp_2Y[(^tBuN)_2C^nBu]$ (Y−N1 and Y−N2, 2.301(3) and 2.302(3) C1−N1).[18] This may be attributed to the larger steric hindrance of Tp^{Me2} compared with the Cp group, which decreases the interaction of the Y and N atoms.

As shown in Figure 6, a new thioamido ligand $[SC(CH_2Ph)NPh]^-$ was formed in **4** by the insertion of one isothiocyanate into the yttrium-benzyl bond and contacted with the yttrium atom in an expected κ^2-bonding mode. The corresponding bond distances (N7−C1 and S1−C1, 1.297(5) and 1.731(5) Å) also suggest substantial electronic delocalization over the $S\ddot{-}C\ddot{-}N$ unit. Moreover, the Y1−N7 and Y1−S1 distances, 2.433(3) Å and 2.8109(16) Å, are similar to those corresponding values found in $(CH_3C_5H_4)_2Y[\kappa^2\text{-}SC(NPh_2)NPh]_2$ (Y−N 2.445(8) Å, Y−S 2.7847(8) Å).[19]

The overall structure of **5** (Figure 7) is very similar to that of **4**, if the difference in the oxygen and sulfur atoms is considered. The newly formed amido ligand is coordinated to the yttrium atom in a κ^2-bonding mode, but a weak interaction between Y1 and C21 (2.735(5) Å) is also observed. The bond parameters around the center carbon atom C21 (N7−C21 and O1−C21, 1.299(6) and 1.276(6)Å) indicated that the $|\bar{O}\ddot{-}\bar{C}\ddot{-}N|$ unit is a delocalized entity as well.[20]

As shown in Figure 8, **6** is a solvent-free monomer. The coordination polyhedron formed in **6** has previously been observed in $(Tp_{Me2})_2U(\kappa^2\text{-}S_2CCH_2Ph)$.[17] There is the expected pattern of delocalization within the YS_2C ring. The dithiocarboxylate ligand is symmetrically coordinated to the Y atom, and the Y−S and S−C bond lengths (2.833(1), 1.682(3) Å) are comparable with those found in $(Me_5C_5)_2Sm(\kappa^2\text{-}S_2CCH{=}CHCH_3)$ (2.790(3)−2.857(3), 1.679(14)−1.720(13) Å), respectively.[21]

Reactions of 2 with RNCNR and PhNCS. The organolanthanide-catalyzed nucleophilic addition of terminal alkynes to carbodiimides offers a straightforward, atom-economic route to the preparation of *N*,*N*′-disubstituted propiolamidines (RN=C(C≡CR′)(NHR)).[22] In this catalytic cycle, a key

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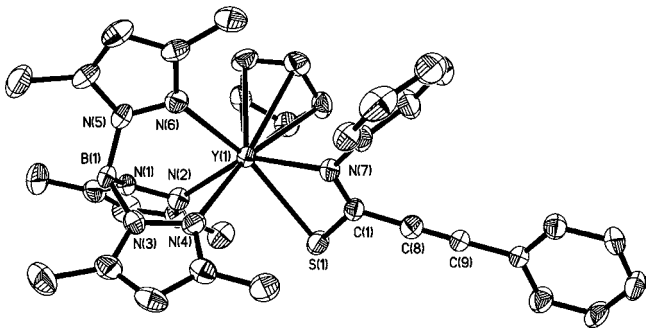
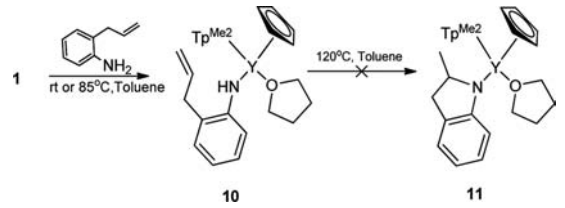


Figure 11. ORTEP diagram of complex **9** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−N7 2.426(5), Y1−S1 2.8091(19), Y1−C1 2.972(6), S1−C1 1.718(6), N7−C1 1.296(8), C1−C8 1.444(9), C8−C9 1.183(8), C9−C8−C1 178.9(7), C8−C1−S1 117.6(5), N7−C1−S1 119.7(5), N7−C1−C8 122.6(6), Y1−N7−C1 101.6(4), Y1−S1−C1 78.0(2), N7−Y1−S1 59.41(13), Y1−C1−C8 170.7(5).

Scheme 4



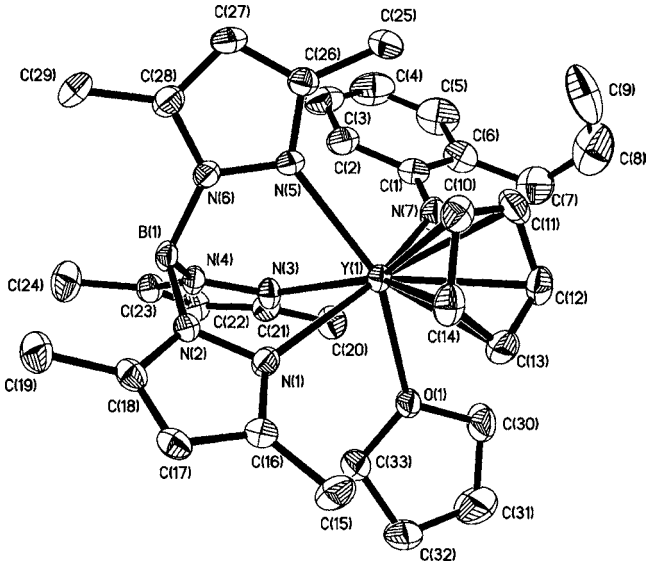


Figure 12. ORTEP diagram of complex **10** with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N7−C1 1.373(9), C8−C9 1.213(18), Y1−N7 2.257(5), Y1−N5 2.436(5), Y1−O1 2.438(4), Y1−N3 2.503(5), Y1−N1 2.561(5), Y1−N7−C1 141.9(5).

step is the insertion of carbodiimide into the lanthanide−alkynyl bond. So, we further investigated the stoichiometric reaction of **2** with carbodiimides, and found that **2** reacted with RN═C═NR (R = ^{i}Pr, Cy) in THF at room temperature to form (Tp^{Me2})CpY[(RN)$_2$CC≡CPh] (R = ^{i}Pr(**7a**), Cy(**7b**)) in almost quantitative yields. Then, the catalytic coupling of carbodiimines and phenylacetylene with 3 mol % of **1** as a catalyst was conducted in THF at 80 °C for 3 h or in toluene at 110 °C for 2 h (Scheme 3) to produce the expected *N*,*N*′-disubstituted propiolamidines RN═C(C≡CPh)(NHR) (R = ^{i}Pr (**8a**), Cy(**8b**)) in >95% isolated yields, which are confirmed by ^{1}H NMR spectroscopy and GC-MS.[22] A plausible mechanism for the formation of **8** is shown in Scheme 3. The protonolysis reaction of **1** and phenylacetylene yields straightforwardly an alkynide species **2**. Nucleophilic addition of **2** to carbodiimide affords the amidinate species **7**. Protonolysis of **7** with alkyne would yield the corresponding amidine **8**, accompanying the regeneration of the alkynide **2**. Consistent with this suggestion, the cross-coupling of carbodiimines and phenylacetylene can also occur smoothly in the presence of 3 mol % of **2** in toluene at 110 °C.

Positive structural verification of **7a** and **7b** was also provided by a single-crystal X-ray analysis (Figures 9 and 10) and showed that the newly formed propiolamidinate ligands [(RN)$_2$CC≡CPh] in **7a** (R = ^{i}Pr) and **7b** (R = Cy) are coordinated to the yttrium atom in an η^2 fashion, similar to that found in [Me$_2$Si(C$_5$Me$_4$)(NPh)]Y[(^{t}BuN)$_2$CC≡CPh].[22a] The bond distances of C−C (C22−C23 1.190(7) Å in **7a**, C34−C35 1.194(6) Å in **7b**) are comparable to the values accepted for the C≡C triplet bond (1.10−1.23 Å).[16]

Attempts to catalyze the cross-coupling of phenyl isothiocyanate and phenylacetylene using 3 mol % of **1** or **2** as a catalyst in toluene at 110 °C were unsuccessful. However, phenyl isothiocyanate could also undergo the stoichiometric yttrium−alkynyl bond insertion with **2** in THF at room temperature, affording (Tp^{Me2})CpY[SC(C≡CPh)NPh] (**9**) in 89% isolated yield. The structure of **9** (Figure 11) is similar to that of **4**, except for the difference of the PhC≡C and PhCH$_2$ groups. The C8−C9 distance (1.183(8) Å) is in the normal range of the C≡C triple bond.[16] To the best of our knowledge, **9** is the first example of isothiocyanate insertion into Ln−C (alkynyl) bonds of organolanthanide alkynyl complexes.

Reaction of 1 with *o*-Allylaniline. The intramolecular hydroamination/cyclization of aminoalkenes represents a straightforward, atom-economic route to the construction of azacyclic skeletons.[23] Encouraged by the above results, we further examined the catalytic activity of **1** for the intramolecular hydroamination/cyclization of aminoalkene. Unfortunately, **1** did not catalyze the hydromination/cyclization of *o*-allylaniline (*o*-NH$_2$C$_6$H$_4$CH$_2$CH═CH$_2$) under the conditions involved (in THF at 85 °C or in toluene at 120 °C). Furthermore, treatment of **1** with 1 equiv of *o*-allylaniline in THF at room temperature afforded only the benzyl abstraction product (Tp^{Me2})CpY(NHC$_6$H$_4$CH$_2$CH═CH$_2$-*o*)(THF) (**10**) in 84% isolated yield. Heating a toluene solution of **10** at 120 °C overnight did not afford the expected hydroamination/cyclization product **11** (Scheme 4). This might suggest that the large steric hindrance of the Tp^{Me2} ligand prevents the coordination of alkene to metal and subsequent insertion into the Ln−N bond. The crystal structure of **10** also shows that the alkene group is away from the yttrium center.

In the ^{1}H NMR spectra of **10**, one multiple peak at 4.94−5.14 ppm is assigned to three hydrogen atoms of the olefin. Moreover, one broad peak at 5.74 ppm was assigned to N*H*, and the characteristic peaks for the benzyl group in **1** have also disappeared.

Complex **10** (Figure 12) is a THF-solvated monomer. The Y1−N7 bond length (2.257(5) Å) is in the range of the Y−N single bond distance and slightly longer than the corresponding values found in (MeCp)$_2$Y(NHC$_6$H$_3$Me$_2$-2,6)(THF) (Y−N1 2.241(4) Å)[24a] and [η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)-

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$(C_2B_{10}H_{10})]Y(NHC_6H_3{}^tBu_2\text{-}2,5)(\mu\text{-}Cl)Li(THF)_3$ (Y−N1 2.222(9) Å).[24b] This may be attributed to the larger steric hindrance of mixed Tp^{Me2}/Cp compared to the corresponding moiety of the latter in the systems.

CONCLUSIONS

In summary, the mixed Tp^{Me2}/Cp-supported yttrium benzyl complex **1** has been synthesized from the corresponding chloride precursor $(Tp^{Me2})CpYCl(THF)$. Protonolysis of **1** with phenylacetylene and *o*-allylaniline gives the corresponding alkynyl and amido derivatives **2** and **10**, respectively. It has been found that complexes **1** and **2** exhibit high reactivity toward a series of unsaturated substrates such as carbodiimides, isocyanate, isothiocyanate, and CS_2. These small molecules readily insert into the Y−C σ bond of **1** to form the corresponding amidinate, amido, thioamido, and dithiocarboxylate complexes, respectively. Furthermore, **1** is an excellent catalyst for the cross-coupling reaction of carbodiimides with phenylacetylene. However, **1** is inefficient for catalyzing both the cross-coupling of phenyl isothiocyanate with phenylacetylene and the intramolecular hydroamination/cyclization of *o*-allylaniline. These results indicate that the introduction of the cyclopentadienyl ligand stabilizes the Tp^{Me2} ligand on yttrium form degradation and impart a marked reactivity to the corresponding lanthanide benzyl complexes with respect to the insertion reactions of small unsaturated molecules across the Ln−C bond.

ASSOCIATED CONTENT

Supporting Information

Tables of atomic coordinates and thermal parameters, all bond distances and angles, and experimental data for all structurally characterized complexes (a CIF file and a PDF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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