New J Chem

The Supporting Information

Mono- and bis- *N*-heterocyclic carbene tantalum, niobium complexes with high oxidation state

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NMR Spectra

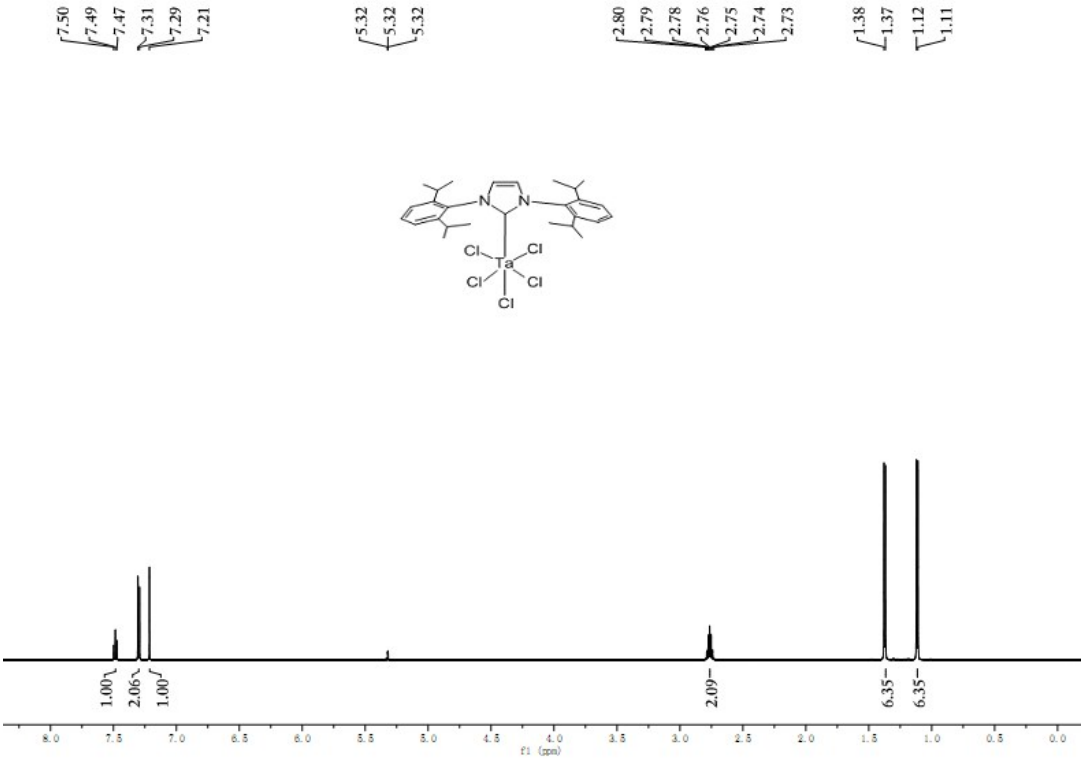

Figure S1 ^{1}H NMR (600 MHz, CD_2Cl_2) for NHCs complex **1**

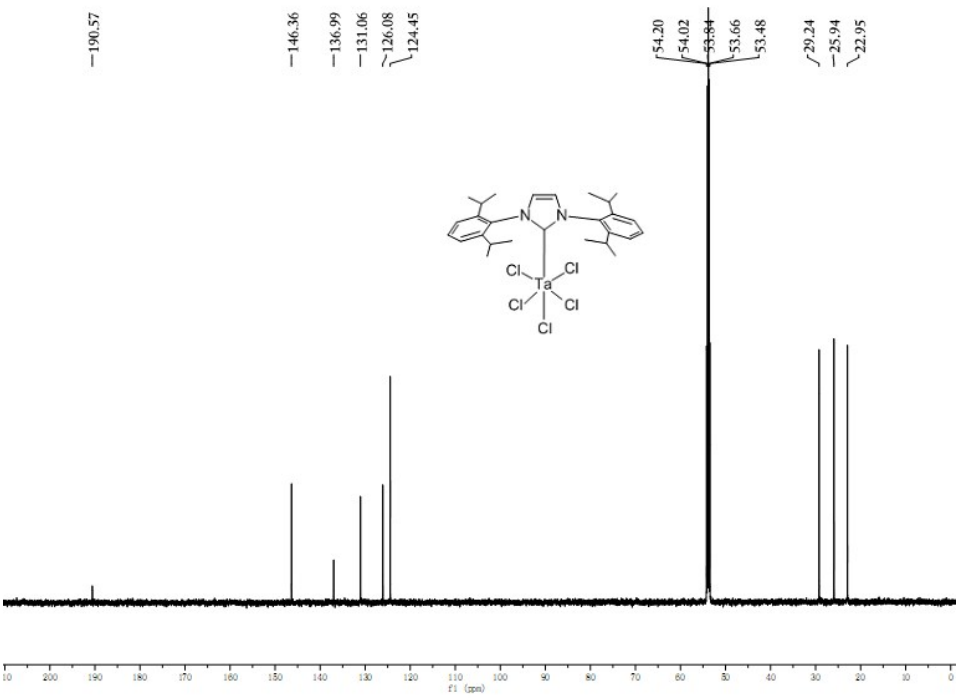

Figure S2 $^{13}C\{^{1}H\}$ NMR (150 MHz, CD_2Cl_2) for NHCs complex **1**

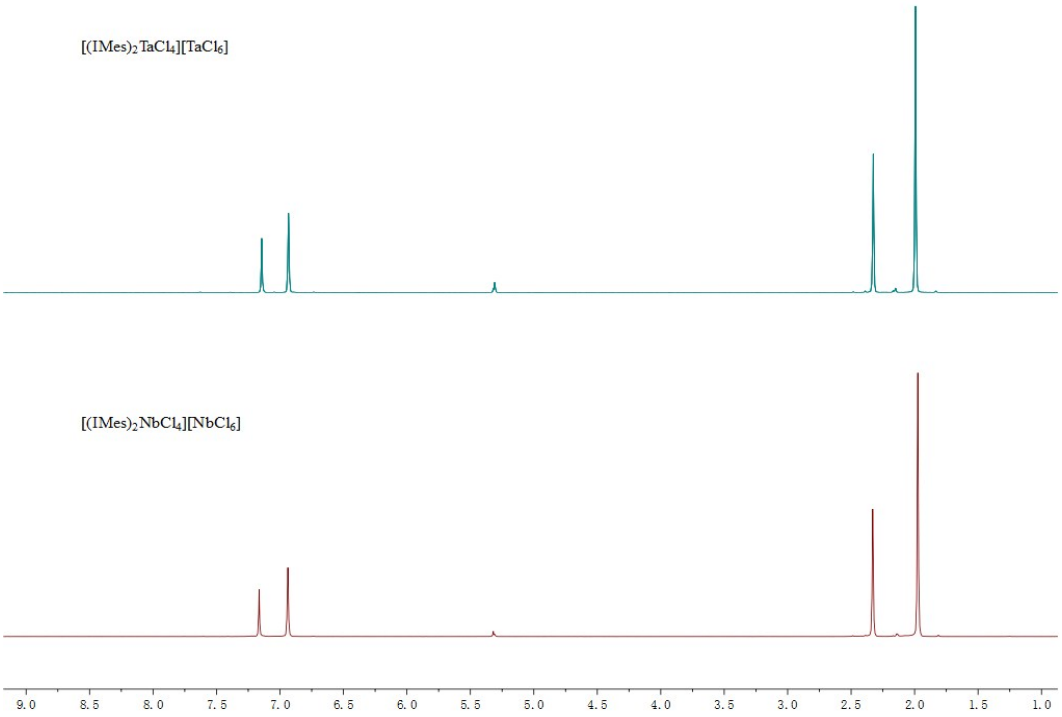

Figure S3 the ^{1}H NMR spectra of complexes **2** and **3**

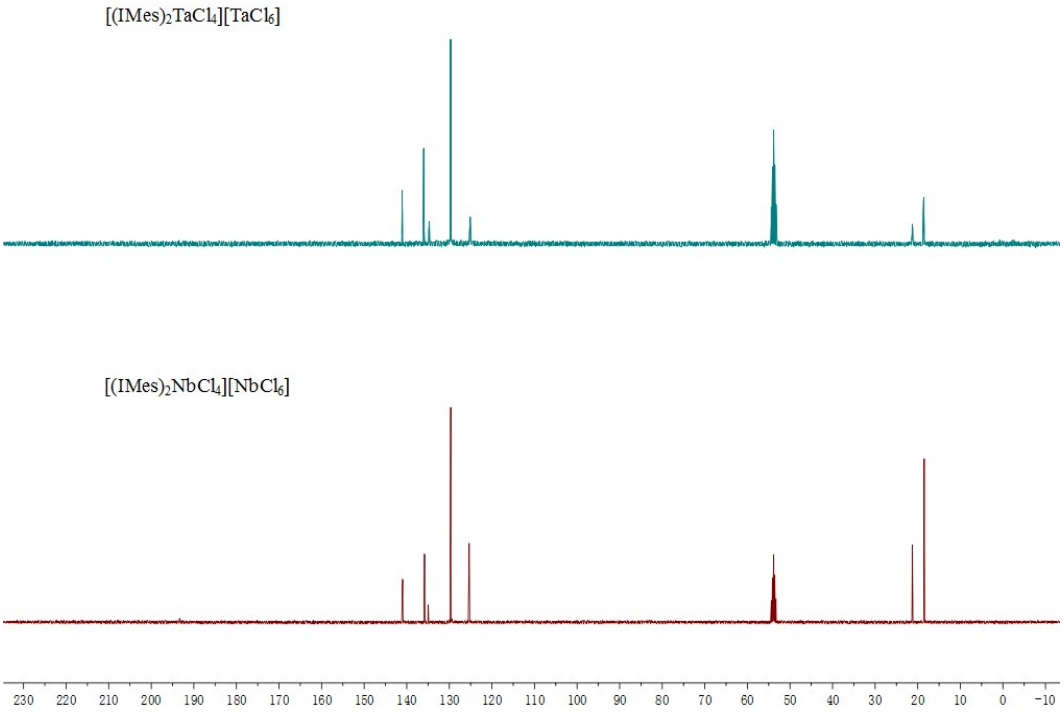

Figure S4 the ^{13}C NMR spectra of complexes **2** and **3**

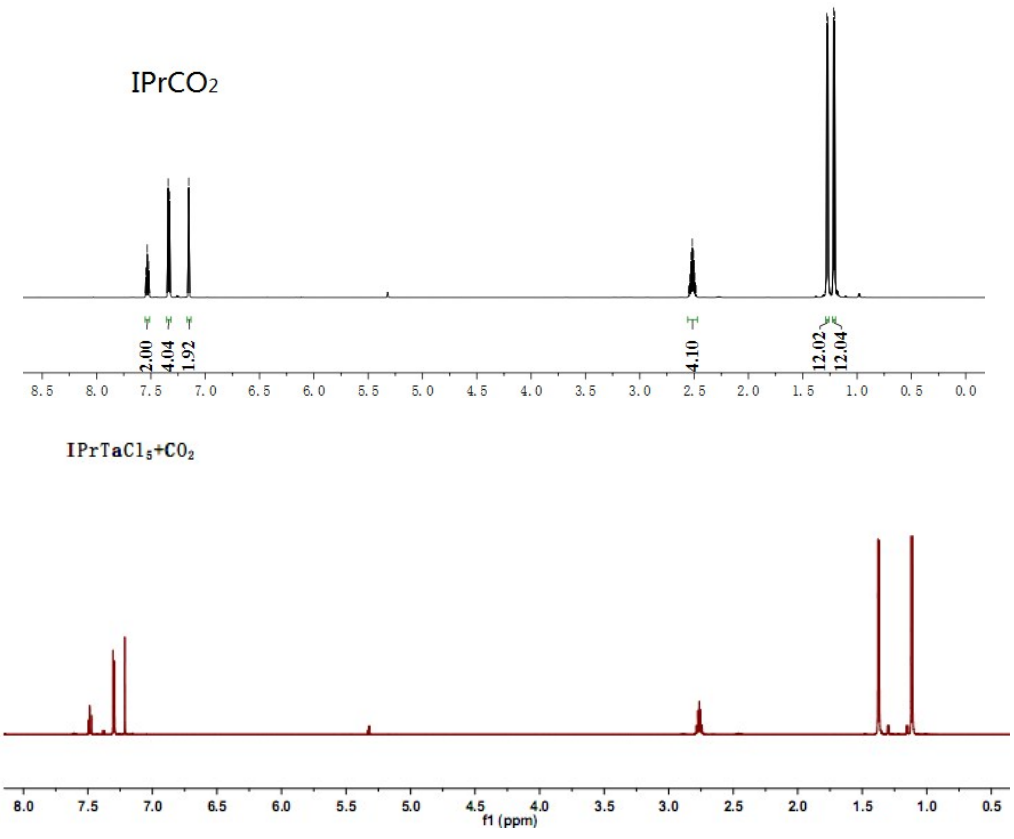

Figure S5 ^{1}H NMR spectra monitored the reaction of **1** with CO_2 in CD_2Cl_2.

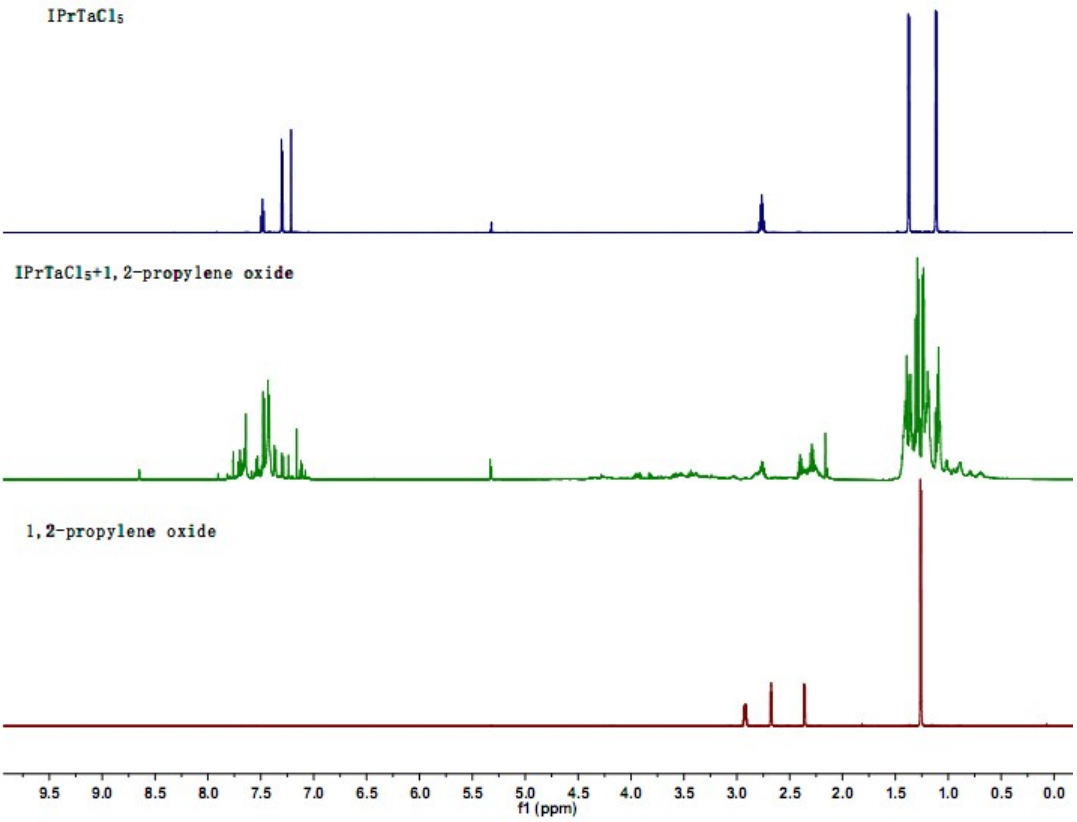

Figure S6 ^{1}H NMR spectra monitored the reaction of **1** with 1,2-propylene oxide in CD_2Cl_2.

UV-vis spectra

The absorption spectra of complexes **1**–**3** in CH_2Cl_2 are shown in Figure S5. The strong absorption peaks at 245 and 266 nm for **1** and **2**, and at 230, 294 nm for **3** are assigned to π–π* transitions of the NHC rings transitions. The shoulder peaks at 290, 360 nm for complexes **1** and **2**, and 323, 367 nm for complex **3** are possibly assigned to the ligand to metal charge transfer (LMCT) absorption. In the long wave length range, there were not observed the absorption in complexes **1**–**3**.

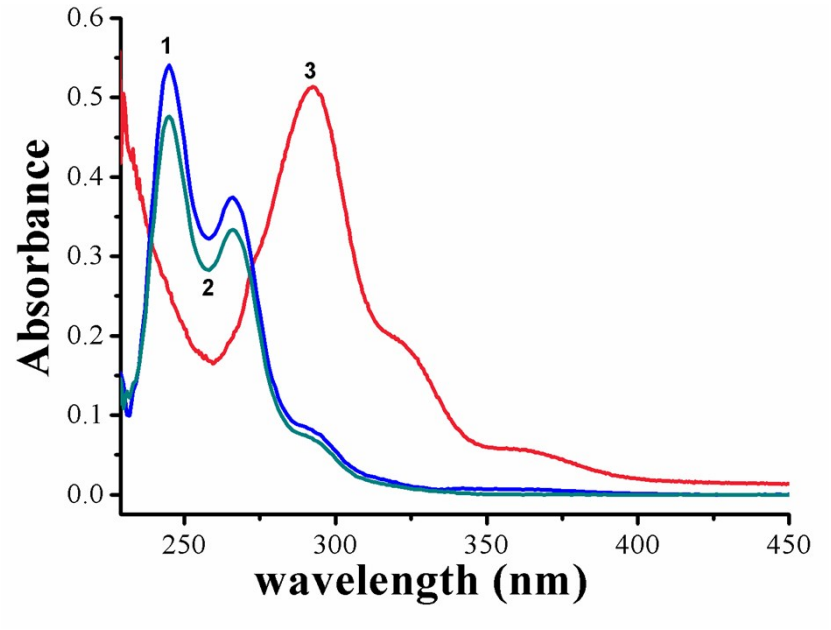

Figure S7 UV–vis absorptions of complexes **1**–**3** (1.0×10^{-4} mol L^{-1} in CH_2Cl_2)

DFT calculation:

DFT calculations (lanl2dz basis set for Ta atom, 6-31+G(d,p) basis set for other atoms, B3LYP method) were performed for [(IPr)$TaCl_5$].

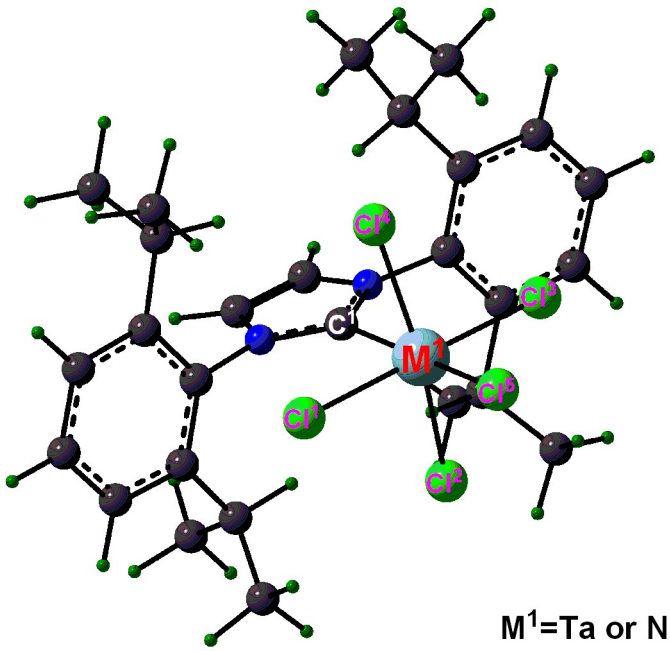

Figure S8 calculated molecular structure of complex **1**. Selected bond lengths (Å) and

angles (°): Ta-C^1 = 2.424, Ta-Cl^1 = 2.352, Ta-Cl^2 = 2.369, C^1-Cl^2 = 3.167, C^1-Cl^4 = 3.167, C^1-Ta-Cl^2 = 82.70, C^1-Ta-Cl^4 = 82.73.

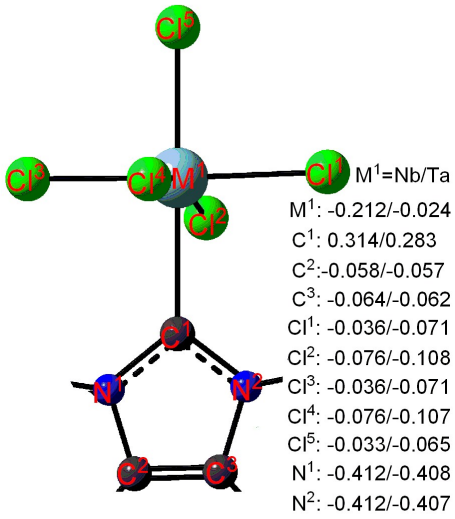

Figure S9 the Natural Bond Orbital charges of $IPrMCl_5$ (M = Ta, or Nb).

X-ray Crystallography

Table S1 Bond lengths (Å) and angles (°) for complex **1**.

Compound **1**

Ta(1)-Cl(1)	2.2989(16)	Ta(1)-Cl(5)	2.3023(15)
Ta(1)-Cl(4)	2.3259(19)	Ta(1)-Cl(2)	2.3557(16)
Ta(1)-Cl(3)	2.3220(18)	Ta(1)-C(15)	2.373(5)
Cl(1)-Ta(1)-Cl(5)	177.75(6)	Cl(1)-Ta(1)-Cl(4)	89.87(7)
Cl(1)-Ta(1)-Cl(3)	90.29(7)	Cl(5)-Ta(1)-Cl(4)	89.85(7)
Cl(5)-Ta(1)-Cl(3)	90.38(7)	Cl(3)-Ta(1)-Cl(4)	169.93(6)
Cl(1)-Ta(1)-Cl(2)	88.07(6)	Cl(4)-Ta(1)-Cl(2)	94.63(7)
Cl(5)-Ta(1)-Cl(2)	89.73(6)	Cl(3)-Ta(1)-C(15)	84.48(12)
Cl(3)-Ta(1)-Cl(2)	95.44(7)	Cl(4)-Ta(1)-C(15)	85.45(13)
Cl(2)-Ta(1)-C(15)	179.32(12)	Cl(5)-Ta(1)-C(15)	90.95(12)
Cl(1)-Ta(1)-C(15)	91.26(12)		

Table S2 Bond lengths (Å) and angles (°) for complexes **2** and **3**.

Compound **2**		Compound **3**	
Ta(1)-Cl(1)	2.2837(19)	Nb(1)-Cl(1)	2.277(7)
Ta(1)-Cl(2)	2.3056(18)	Nb(1)-Cl(2)	2.3107(11)
Ta(1)-Cl(3)	2.2985(18)	Nb(1)-Cl(3)	2.278(11)
Ta(1)-Cl(4)	2.2811(19)	Nb(1)-Cl(4)	2.2952(12)
Ta(1)-C(10)	2.346(6)	Nb(1)-C(10)	2.352(4)
Ta(1)-C(31)	2.336(6)	Nb(1)-C(33)	2.356(4)
Cl(4)-Ta(1)-Cl(3)	91.42(9)	Cl(3)-Nb(1)-Cl(4)	94.7(3)
Cl(4)-Ta(1)-Cl(2)	166.64(7)	Cl(4)-Nb(1)-Cl(2)	89.53(5)
Cl(3)-Ta(1)-Cl(2)	89.56(8)	Cl(3)-Nb(1)-Cl(2)	166.0(3)
Cl(1)-Ta(1)-C(31)	83.44(16)	Cl(1)-Nb(1)-C(33)	95.7(2)
Cl(2)-Ta(1)-C(31)	99.22(16)	Cl(2)-Nb(1)-C(33)	83.61(9)
Cl(1)-Ta(1)-C(10)	94.72(16)	Cl(1)-Nb(1)-C(10)	81.9(2)
Cl(2)-Ta(1)-C(10)	84.34(16)	Cl(2)-Nb(1)-C(10)	100.96(10)
Cl(4)-Ta(1)-Cl(1)	92.12(10)	Cl(1)-Nb(1)-Cl(4)	165.2(2)
Cl(1)-Ta(1)-Cl(3)	168.20(7)	Cl(3)-Nb(1)-Cl(1)	91.7(3)
Cl(1)-Ta(1)-Cl(2)	89.60(9)	Cl(1)-Nb(1)-Cl(2)	87.5(2)
Cl(4)-Ta(1)-C(31)	94.14(16)	Cl(4)-Nb(1)-C(33)	98.27(10)
Cl(3)-Ta(1)-C(31)	85.07(16)	Cl(3)-Nb(1)-C(33)	82.5(3)
Cl(4)-Ta(1)-C(10)	82.32(16)	Cl(4)-Nb(1)-C(10)	84.55(10)
Cl(3)-Ta(1)-C(10)	96.91(16)	Cl(3)-Nb(1)-C(10)	92.8(3)
C(31)-Ta(1)-C(10)	176.0(2)	C(10)-Nb(1)-C(33)	174.70(13)