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Structural and Electronic Non-innocence of α-Diimine Ligands on Niobium for Reductive C-Cl Bond Activation and Catalytic Radical Addition Reactions

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Abstract

A d^0 niobium(V) complex, $NbCl_3$(α-diimine) (**1a**), supported by a dianionic redox-active *N*,*N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-2,3-dimethyl-1,3-butadiene (α-diimine) ligand (ene-diamido ligand) served as a catalyst for radical addition reactions of CCl_4 to α-olefins and cyclic alkenes, selectively affording 1:1 radical addition products in a regioselective manner. During the catalytic reaction, the α-diimine ligand smoothly released and stored an electron to control the oxidation state of the niobium center by changing between an η^4-(σ^2,π) coordination mode with a folded MN_2C_2 metallacycle and a κ^2-(*N*,*N'*) coordination mode with a planar MN_2C_2 metallacycle. Kinetic studies of the catalytic reaction elucidated the reaction order in the catalytic cycle: the radical addition reaction rate obeyed first-order kinetics that were dependent on the concentrations of the catalyst, styrene, and CCl_4, while a saturation effect was observed at a high CCl_4 concentration. In the presence of excess amounts of styrene, styrene coordinated in an η^2-olefinic manner to the niobium center to decrease the reaction rate. No observation of oligomers or polymers of styrene and high stereoselectivity for the radical addition reaction of CCl_4 to cyclopentene suggested that the C—C bond formation proceeded inside the coordination sphere of niobium, which was in good accordance with the negative entropy value of the radical addition reaction. Furthermore, reaction of **1a** with (bromomethyl)cyclopropane confirmed that both the C—Br bond activation and formation proceeded on the α-diimine-coordinated niobium center during transformation of the cyclopropylmethyl radical to a homoallyl radical. With regard to the reaction mechanism, we detected and isolated $NbCl_4$(α-diimine) (**6a**) as a transient one-electron oxidized species of **1a** during reductive cleavage of the C—X bonds; in addition, the monoanionic α-diimine ligand of

6a adopted a monoanionic canonical form with selective one-electron oxidation of the dianionic ene-diamido form of the ligand in **1a**.

Introduction

Organic radicals are among the most useful reactive species for carbon-carbon bond formation in synthetic organic chemistry.[1] Over the last several decades, organic radicals have been accessed by treating alkyl halides with a wide variety of radical initiators such as AIBN, BEt_3, and peroxides:[2] Kharasch *et al.* first discovered that organic radicals generated *in situ* from homolytic cleavage of the carbon-halogen bonds of alkyl halides by these typical radical initiators added across double bonds of olefins.[3] Later, one-electron redox processes on metal centers were determined to be an effective method for generating radical species from alkyl halides smoothly and controllably, while also suppressing side reactions such as oligomerization and telomerization of olefins.[4-12] Remarkable research efforts have been devoted to atom transfer radical addition (ATRA) and polymerization (ATRP), in which a radical generation step can be finely controlled through modulation of the supporting ligand framework in transition metal complexes to tune redox processes at the metal center.[6c-k,8c,9f,h,10,13] A recent trend is directed toward the introduction of redox-active ligands around transition metals to avoid any change in the oxidation state at the metal center.[14-17] In a representative example reported by Chirik and coworkers, [2+2] cycloaddition reactions were catalyzed by {bis(imino)pyridine}iron(II) complexes,[14b,15a-d] where the ligand reversibly changed from dianionic to neutral during the reductive cyclization process. Another typical example was reported by Heyduk and coworkers for the catalytic application of d^0 bis(*ortho*-aminophenolate)zirconium complexes to the disproportionation of diphenylhydrazine to a mixture of aniline and azobenzene.[17b] The tetranionic bis(*ortho*-aminophenolate) ligand provided the two electrons needed to cleave the N—N bond, while allowing the zirconium center to remain in the d^0

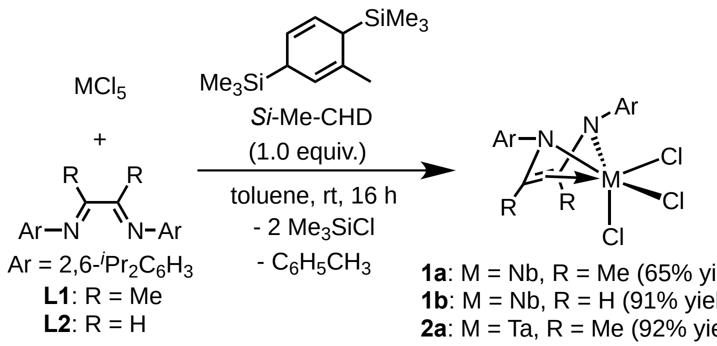
oxidation state. Based on these results, we anticipated that systems incorporating redox-active ligands coordinated to early transition metal d^0 centers could efficiently support catalytic radical addition involving reversible one-electron redox processes.

As exemplified in these two seminal examples, the redox-active ligands often contain planar π-conjugated frameworks that effectively overlap with a d-orbital of the central metal, allowing for reduction or oxidation of substrates occurring at the metal center to be mediated by the redox-active ligand without formal oxidation state change at the metal center. We have investigated the structurally and electronically flexible coordination behavior of the redox-active α-diimine ligand to early transition metals, in which the α-diimine ligand coordinates to the metal in either folded η^4-(σ^2,π) coordination or planar κ^2-(*N*,*N'*) coordination modes.[18] Herein, we report the application of group 5 metal d^0 complexes MCl_3(α-diimine) [M = Nb and Ta; α-diimine = *N*,*N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-2,3-dimethyl-1,3-butadiene (**L1**) and *N*,*N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (**L2**)] as catalysts for radical addition reaction of alkyl halides to alkenes. The major role of the α-diimine ligand was to release and store one-electron during the catalytic reaction by reversibly switching the folding η^4-(σ^2,π) coordination and planar κ^2-(*N*,*N'*) coordination to the metal center, in which the planar κ^2-(*N*,*N'*) coordination mode smoothly transferred one-electron from the ligand to the niobium center to generate Nb(IV) for accelerating the reductive cleavage of the C—Cl bond. Structural change induced electron transfer between the metal center and the redox-active ligand is a new strategy for organizing various catalytic reactions by metal complexes with redox-active ligands. Kinetic studies for the radical addition reaction as well as control experiments were performed to elucidate the reaction mechanism.

Results and Discussion

Trichloroniobium complexes with ene-diamido ligands

Niobium and tantalum complexes MCl_3(α-diimine) (**1a**: M = Nb, α-diimine = *N,N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-2,3-dimethyl-1,3-butadiene (**L1**); **1b**: M = Nb, α-diimine = *N,N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (**L2**); **2a**: M = Ta, α-diimine = **L1**; **2b**: M = Ta, α-diimine = **L2**) were prepared by reducing MCl_5 (M = Nb and Ta) with 1.0 equiv. of 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (*Si*-Me-CHD) in the presence of the corresponding α-diimine (**L1** and **L2**) in toluene (eq 1).[18i] The α-diimine ligands in **1a** and **1b** coordinated to the niobium atom in a dianionic ene-diamide manner, as confirmed by the ^1H and $^{13}C\{^1H\}$ NMR spectra. In the $^{13}C\{^1H\}$ NMR spectra of **1a** and **1b**, a signal assignable to the olefinic carbons of the ene-diamido ligands was observed at δ_C 110.8 for **1a** and 103.8 for **1b**, and the ^1H NMR spectrum of **1b** displayed one singlet signal for the imine protons of **L2**, which was shifted to a higher field (δ_H 5.76). Figure 1 shows an ORTEP drawing of complex **1a**, and the bond distances and angles of **1a** are summarized in Table 1. The lengths of C1—N1 [1.389(2) Å] and C2—N2 [1.410(3) Å] are longer than those of typical C=N double bonds and closer to those of the typical C—N single bonds, while the length of C1—C2 [1.383(2) Å] is between that of C=C double and C—C single bonds. The 5-membered chelate ring is folded with dihedral angles between the N1—C1—C2—N2 and N1—Nb—N2 planes of 126.17(8)° for **1a** and 121.8(3)° for **1b**, suggesting that the C1—C2 double bond coordinates through π-donation to the niobium center in a η^4-(σ^2,π) coordination mode, which were typical for dianionic ligation of the ene-diamido ligands to group 5 metal centers.[18b,e,i,19] In sharp contrast to the folded structure observed for **1a** and **1b**, the fold angle of the MN_2C_2 ring for monoanionic α-diimine complexes (including **6a**, *vide infra*) is typically in the range of 164—179°.[18b,e,f,h,i,20] Although we considered that **1a** was a Nb(V) species bearing a dianionic ene-diamido ligand, we could not completely exclude the contribution of a Nb(IV) species having a monoanionic α-diimine ligand in **1a**. The ^{1}H NMR spectrum of **1a** in toluene-d_8 at room temperature showed a singlet peak at 1.85 ppm for *Me*C=C*Me*, while only the peak shifted to 1.53 ppm at -80 ºC (Figure S3), suggesting that there was a small contribution of the singlet/triplet niobium complexes, Nb(IV) species having α-diimine monoanionic ligands.[21] Niobium complexes **1a** and **1b** were close structural analogs to the previously reported tantalum complexes **2a** and **2b**.[18i]



(1)

1a: M = Nb, R = Me (65% yield)
1b: M = Nb, R = H (91% yield)
2a: M = Ta, R = Me (92% yield)
2b: M = Ta, R = H (86% yield)

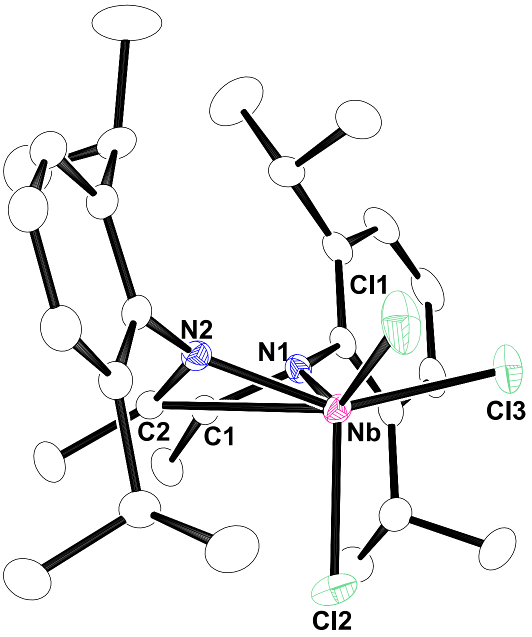


Figure 1. Molecular structure of **1a** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

Table 1. Selected bond distances (Å) and angles (deg.) of **1a**.

Nb—N1	1.9692(16)	Nb—C2	2.4810(17)
Nb—N2	1.9901(16)	N1—C1	1.389(2)
Nb—Cl1	2.3873(7)	N2—C2	1.383(2)
Nb—Cl2	2.3050(6)	C1—C2	1.410(3)
Nb—Cl3	2.3892(8)	N1—Nb—N2	86.66(6)
Nb—C1	2.4747(17)	ene-diamido fold angle[a]	126.17(8)

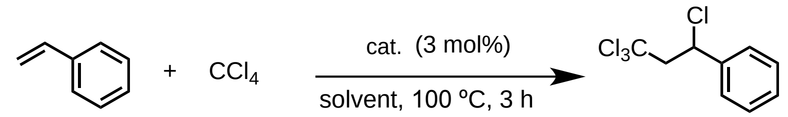
[a] ene-diamido fold angle: dihedral angle between N1—C1—C2—N2 and N1—Nb—N2 planes

Catalytic radical addition reactions

We found that **1a** exhibited catalytic activity for radical addition reactions of CCl_4 to various alkenes. A reaction of CCl_4 and styrene (**3a**) was chosen as a model radical addition reaction to evaluate the optimum catalytic conditions. First, niobium and tantalum complexes **1a**,**1b**, and **2a**,**2b** were screened as catalysts (3 mol%) for radical addition of CCl_4 (1.50 mmol, 5.0 equiv.) to **3a** (0.300 mmol, 1.0 equiv.) in C_6D_6 (0.30 mL) at 100 °C for 3 h in J-Young NMR tubes; the results are shown in Table 2. Niobium complex **1a** exhibited excellent catalytic activity for the radical addition reaction, selectively affording a 1:1 coupling product, 1,3,3,3-tetrachloropropylbenzene (**4a**), in quantitative yield without any byproducts, such as styrene oligomers, polystyrene, or other regioisomers of the radical addition product (entry 1). Niobium complex **1b** showed less activity, giving **4a** in 60% yield (entry 2), whereas the tantalum complexes **2a** and **2b** produced polystyrene without forming any **4a** (entries 3 and 4). We further examined some low-valent niobium complexes, such as $NbCl_3$(DME) and $NbCl_3$(TMEDA), as catalysts. Although the coordination of 1,2-dimethoxyethane (DME) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) to Nb(III) suppressed the radical polymerization of styrene, $NbCl_3$(DME) had lower catalytic activity for **4a** (55%) than **1a**, and $NbCl_3$(TMEDA) exhibited no catalytic activity (entries 5 and 6). Accordingly, coordination of a dianionic ene-diamido ligand to the Nb(V) moiety played an essential role in the high catalytic activity without any radical polymerization, indicating that the catalytic cycle using **1a** did not involve free organic radicals. In contrast to radical addition catalysts based on late transition metal complexes, such as Ru(III) and Cu(II), the high oxidation state Nb(V) catalyst system did not require any reductant such as AIBN, although the niobium system exhibited lower catalytic activity.[9,10]

We next screened solvents such as toluene, acetonitrile, and THF for this radical addition reaction catalyzed by **1a** (entries 7—9). The coupling product **4a** was quantitatively obtained in toluene-d_8 (entry 7), as in C_6D_6 (entry 1), whereas the reaction in CD_3CN afforded **4a** in lower yield (19%) (entry 8) and no reaction was observed in THF-d_8 (entry 9). Decreasing the amount of CCl_4 from 5.0 equiv. to 3.0 equiv. or 1.0 equiv. lowered the yield of **4a** (entries 10 and 11). Therefore, we employed 5.0 equiv. of CCl_4 for further studies.

Table 2. Catalytic radical addition reaction of CCl_4 to styrene.[a]



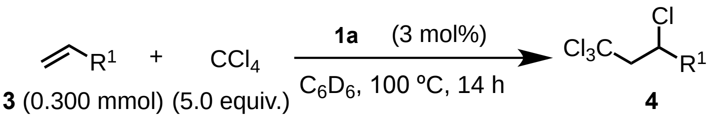
3a (0.300 mmol) (*X* equiv.) **4a**

entry	cat.	solvent	CCl_4 (equiv.)	yield[b] (%)
1	**1a**	C_6D_6	5.0	>99 (97)
2	**1b**	C_6D_6	5.0	60
3	**2a**	C_6D_6	5.0	0
4	**2b**	C_6D_6	5.0	0
5	$NbCl_3$(DME)	C_6D_6	5.0	55
6	$NbCl_3$(TMEDA)	C_6D_6	5.0	0
7	**1a**	toluene-d_8	5.0	>99
8	**1a**	CD_3CN	5.0	19
9	**1a**	THF-d_8	5.0	0
10	**1a**	C_6D_6	3.0	62
11	**1a**	C_6D_6	1.0	33

[a]All reactions were carried out in J-Young NMR tubes. [b]Determined by ^1H NMR analysis using 1,4-dioxane as an internal standard. [c]Isolated yield was given in parentheses.

Complex **1a** (3 mol%) catalyzed the reactions of various alkene substrates **3b**—**j** (0.300 mmol) with CCl_4 (5.0 equiv.) in C_6D_6 at 100 ºC, although a longer reaction time was required than for styrene (Table 3). The 1:1 coupling product **4b** was obtained in 93% yield in the reaction of *para*-methylstyrene **3b**, whereas incorporation of an electron-withdrawing group at the *para*-position of the styrene decreased the yield of the product due to the contamination of oligomers as byproducts (entries 1—3). Reaction with *meta*-methylstyrene **3e** proceeded in 81% yield; but no product was obtained for *ortho*-methylstyrene **3f**, likely due to steric congestion around the alkene moiety (entries 4 and 5). α-Olefins with alkyl substituents were also amenable to the radical addition reactions: alkyl olefins such as 1-octene (**3g**), trimethyl(vinyl)silane (**3h**), vinylcyclohexane (**3i**), and allylbenzene (**3j**) produced the corresponding 1:1 coupling compounds **4g**—**j** in moderate to high yields (entries 6—9).

Table 3. Radical addition reaction of CCl_4 to alkenes.[a]

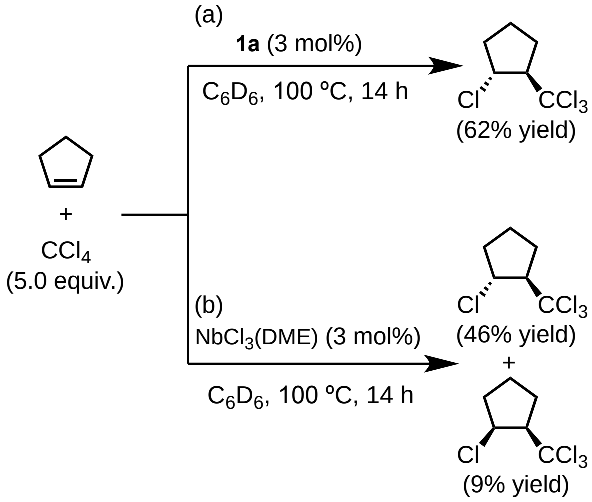


entry	R^1		conv. (%)[b]	yield (%)[b]
1	p-MeC_6H_4	**3b**	94	93 (88)
2	p-ClC_6H_4	**3c**	100	82[d] (78)
3	p-$CF_3C_6H_4$	**3d**	76	40[d] (38)
4	m-MeC_6H_4	**3e**	86	81 (81)
5	o-MeC_6H_4	**3f**	95	0[e]
6	^{n}Hex	**3g**	100	>99 (98)
7	Me_3Si	**3h**	80	77 (70)
8	Cy	**3i**	58	58 (58)
9	$PhCH_2$	**3j**	56	48 (40)

[a] All reactions were carried out in J-Young NMR tubes. [b] Determined by ^1H NMR analysis using 1,4-dioxane as an internal standard. [c] Isolated yield was given in parentheses. [d] Oligomer was observed as byproduct. [e] 1-methyl-2-(3,3,3-trichloroprop-1-en-1-yl)benzene was observed as byproduct.

As shown in Scheme 1, a reaction of cyclopentene with CCl_4 was also catalyzed using either **1a** (3 mol%) or $NbCl_3(DME)$ (3 mol%) in C_6D_6 at 100 ºC for 14 h. The reaction using **1a** afforded only *trans*-1-chloro-2-(trichloromethyl)cyclopentane in 62% yield without contamination by other stereoisomers (Scheme 1a). In contrast, the reaction using $NbCl_3(DME)$ resulted in a 5:1 mixture of *trans*- and *cis*-1-chloro-2-(trichloromethyl)cyclopentane (Scheme 1b), indicating that free radical addition was partially involved in the reaction using $NbCl_3(DME)$ (*vide infra*).[22]

Scheme 1. Radical addition reaction of CCl_4 to cyclopentene catalyzed by (a) **1a** and (b) $NbCl_3(DME)$.



Kinetics of radical addition reactions

To gain further insight into the reaction mechanism, we carried out kinetic experiments for the radical addition reaction of CCl_4 to styrene catalyzed by **1a** at 100 ºC in C_6D_6 with varying concentrations of **1a**, styrene, and CCl_4. The reaction rate constants k_{obs} were determined by monitoring the concentrations of the coupling product **4a** by ^{1}H NMR spectroscopy in C_6D_6 containing hexamethylbenzene as an internal standard. A plot of k_{obs} obtained from six different catalyst concentrations under conditions of $[styrene]_0 = 0.60$ M and $[CCl_4]_0 = 3.0$ M showed a linear (first-order) dependence of the k_{obs} on the concentration of **1a** in a catalyst concentration range of 18—72 mM (Figure 2).

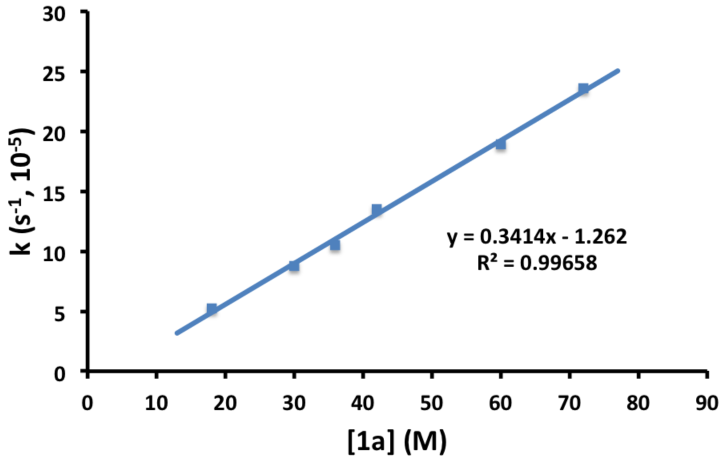


Figure 2. Dependence of k_{obs} on the concentration of **1a** as the catalyst for the radical addition reaction of CCl_4 and styrene. Reaction conditions: $[styrene]_0 = 0.60$ M, $[CCl_4]_0 = 3.0$ M, temperature 100 °C.

Next, we evaluated the effects of $[styrene]_0$ under the conditions of $[CCl_4]_0 = 4.5$ M and $[\mathbf{1a}]_0 = 18$ mM. When $[styrene]_0$ was less than 0.90 M, k_{obs} increased linearly, suggesting that the reaction rate obeyed first-order kinetics depending on the styrene concentration, whereas k_{obs} decreased when the amount of $[styrene]_0$ was greater than 0.90 M (Figure 3). The reaction rate was also slower for 1-octene (Figure S10).[23] In addition, a kinetic studies of CCl_4 to trimethyl(vinyl)silane showed a deviation from linearity (Figure S12).[23] To investigate these observations at higher olefin concentrations, we measured the UV-vis spectra of **1a** in styrene (neat), 1-octene (neat), and trimethyl(vinyl)silane (neat) (Figure 4). A UV-vis spectrum of **1a** in styrene displayed a new absorption ($\lambda_{max} = 748$ nm) characteristic of complexes containing the monoanionic π-radical α-diimine ligand bound to a metal center,[20n,24] as well as a shoulder around 465 nm, which was attributed to the contribution of the filled pπ-orbitals of the nitrogen atoms to a vacant dπ-orbital of the niobium, typically observed for (ene-diamido)metal complexes with planar MN_2C_2 metallacycles.[18b]

These UV-vis spectral data suggested that the coordination mode of the α-diimine in **1a** switched from dianionic η^4-(σ^2,π) coordination to monoanionic κ^2-(*N*,*N'*) -ligation upon interaction with the alkene substrates (eq 2). In addition, the π-acidic character of the coordinating alkenes accelerated the electron transfer from the dianionic ligand to the metal center to form Nb(IV) species **A**, which is in contrast to anionic niobium complexes [^{n}Bu$_4$N][NbCl$_4$(α-diimine)] (**5a**:, α-diimine = **L1**; **5b**: α-diimine = **L2**), where α-diimine coordinated with a κ^2-(*N*,*N'*)-binding mode to the niobium center and showed a typical ligand-to-metal charge-transfer (LMCT) band at 468 nm (see Supporting Information). In the case of 1-octene, an absorption band also appeared at 735 nm, while there was no detectable band in the range of 730—750 nm for the solution of **1a** in trimethyl(vinyl)silane. Furthermore, the different intensities of absorptions in the range of 730—750 nm for these three alkenes were due to the strength of the interaction of the niobium atom with alkenes; accordingly, the order of the observed intensity was 1-octene > styrene > trimethyl(vinyl)silane. This correlated with the change in k_{obs} observed at a higher concentration of alkenes during the reaction kinetics, which also decreased k_{obs} at a high concentration in the order 1-octene > styrene > trimethyl(vinyl)silane. In addition, **1a** partially decomposed in the presence of excess styrene (1.8 M) at 100 °C after 4 h and free ligand **L1** was detected.[25] We thus concluded that a decrease in k_{obs} value was observed when the amount of [styrene] : [CCl$_4$] was greater than [styrene]$_0$: [CCl$_4$]$_0$ = 1 : 5 due to both interaction of **1a** with alkenes and decomposition of **1a**.

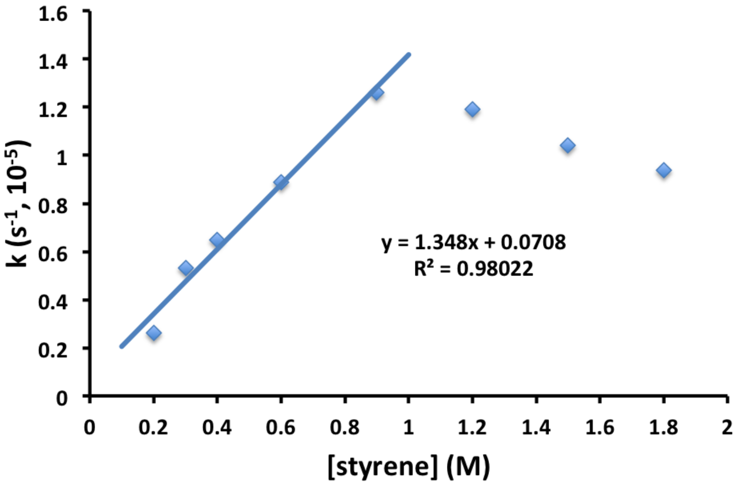


Figure 3. Dependence of k_{obs} on the concentration of styrene for the radical addition reaction of CCl_4 and styrene. Reaction conditions: $[\mathbf{1a}]_0$ = 18 mM, $[CCl_4]_0$ = 4.5 M, temperature 100 ºC.

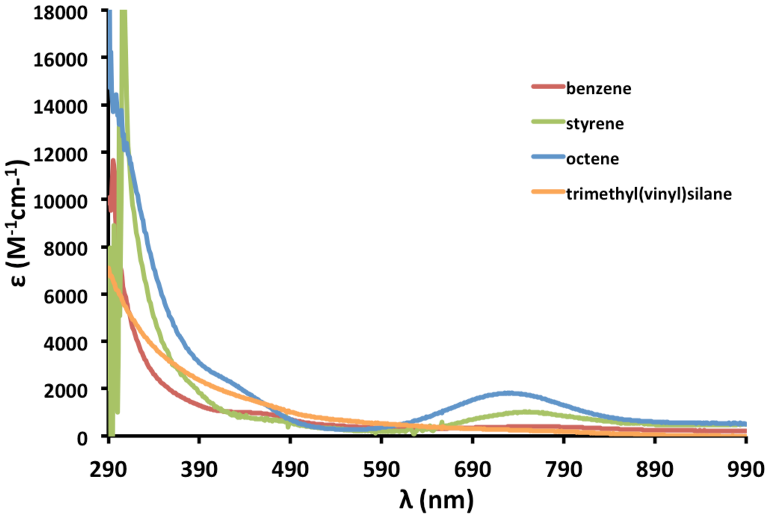
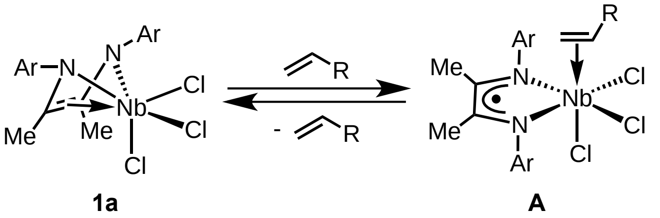


Figure 4. UV-vis spectra of complex **1a** in benzene (red trace), styrene (green trace), 1-octene (blue trace), and trimethyl(vinyl)silane (orange trace).



(2)

Finally, under fixed concentrations of [**1a**]$_0$ = 18 mM and [styrene]$_0$ = 0.60 M, the initial concentration of CCl_4 was changed: the values of k_{obs} for product formation increased linearly up to [CCl_4]$_0$ = 4.8 M, whereas the reaction rate was almost constant when more than 4.8 M of [CCl_4]$_0$ was used (Figure 5). This saturation behavior of the rate constant on CCl_4 concentration can be rationalized by assuming an equilibrium between **1a** and any dormant species involving CCl_4 (*vide infra*).[8a,e] In fact, a solution of **1a** with Ph_2CCl_2 in benzene showed a shoulder at 475 nm due to a LMCT band as well as an absorbance at 760 nm assignable to the band due to the planar-ligated monoanionic α-diimine, which suggested the formation of alkylhalide-coordinated species **B**, as shown in Scheme 2 (*vide infra*).

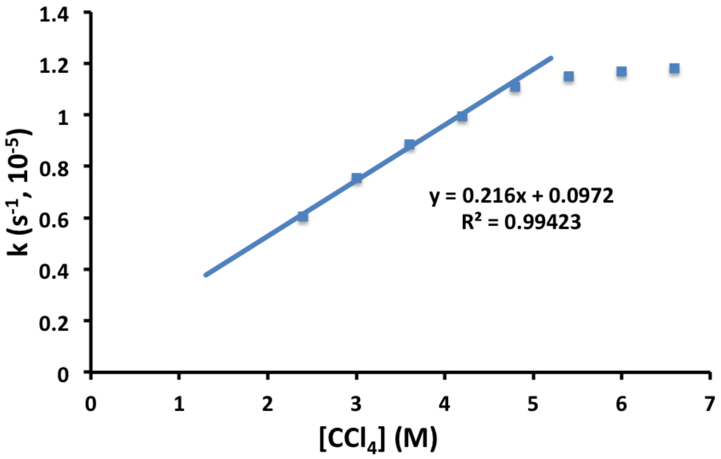


Figure 5. Dependence of k_{obs} on the concentration of CCl_4 for the radical addition reaction of CCl_4 and styrene. Reaction conditions: [**1a**]$_0$ = 18 mM, [styrene]$_0$ = 0.60 M, temperature 100 ºC.

We thus propose the following rate laws based on our kinetic study. First, we show the rate law as eq 3 under the conditions of lower concentrations of both [CCl_4] and [styrene] ([CCl_4] < 4.8 M and [styrene] < 0.90 M). Under these conditions, the reaction rate was first-order for [Nb], [CCl_4], and [styrene].

$$\text{Rate} = k[\text{Nb}][\text{CCl}_4][\text{styrene}] \qquad (3)$$

At the higher concentrations of [CCl_4] ([CCl_4] > 4.8 M), the rate law is given as eq 4, which suggested that the reaction rate was first-order for [Nb] and [styrene], and zero-order for [CCl_4].

$$\text{Rate} = k[\text{Nb}][\text{styrene}] \qquad (4)$$

In the case of a higher concentration of [styrene] ([styrene] > 0.90 M), we cannot clearly show the reaction rate because of the formation of **A** as well as the decomposition of **1a**.

Interaction of 1a with alkenes

As shown in Figure 4, a new absorption band for the solution of **1a** in styrene (neat) and 1-octene (neat) was observed around 740 nm, suggesting that alkenes interacted with the niobium center to induce the planar ligation of **L1** to form **A** having a monoanionic α-diimine.[20n,24] When we monitored a mixture of **1a** (18 mM) and 1-octene (0.90 M) in benzene (1.0 mL) by UV-vis spectroscopy at room temperature, the same absorption band (735 nm) was observed. However, the band decreased upon addition of increasing amounts of CCl_4 (Figure 6). Under the condition, no radical addition product was observed, suggesting that the alkene was replaced to CCl_4. Accordingly, the alkene coordinated species **A** is likely not involved in the catalytic cycle.

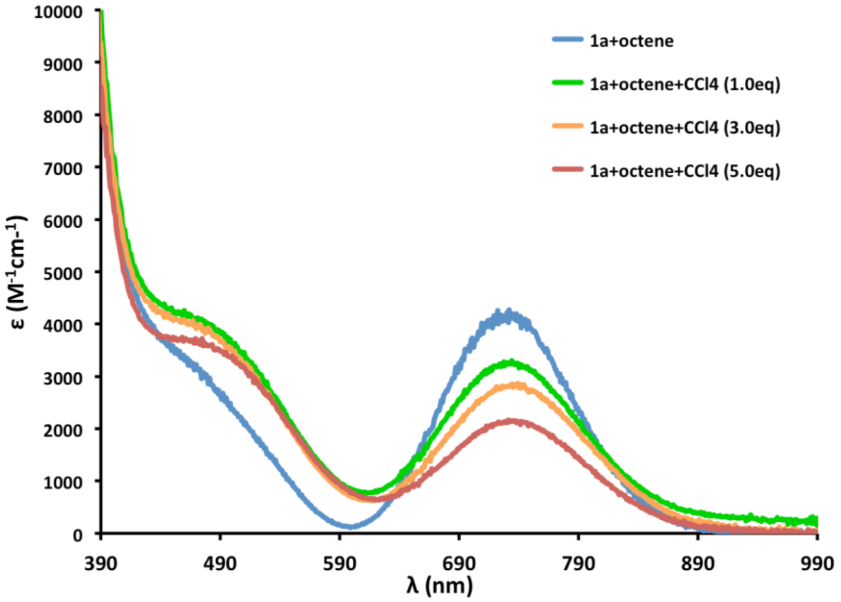
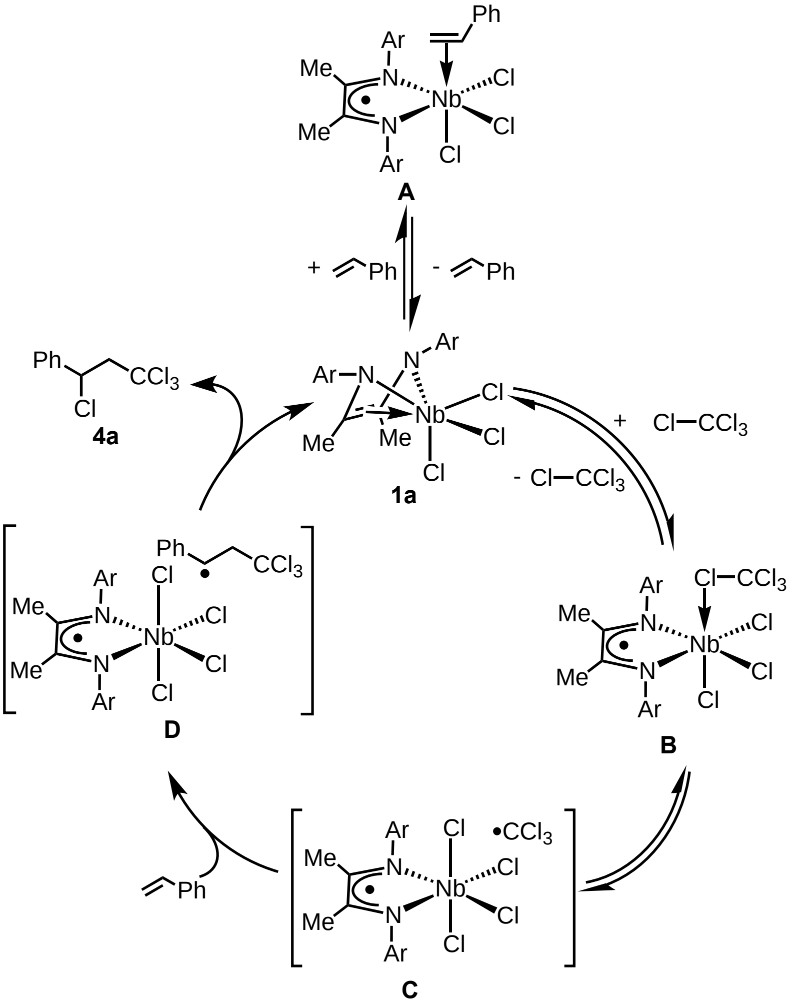


Figure 6. UV-vis spectrum of **1a** (18 mM) in benzene (a) with 1-octene (0.90 M) (blue line), (b) with 1-octene (0.90 M) and CCl_4 (0.90 M) (green line) (c) with 1-octene (0.90 M) and CCl_4 (2.7 M) (orange line), and (d) with 1-octene (0.90 M) and CCl_4 (4.5 M) (red line).

Proposed mechanism of the radical addition reaction

Based on NMR kinetic experiments and UV-vis spectroscopic experiments, we propose a mechanism of the radical addition reaction for styrene as outlined in Scheme 2. Initially, CCl_4 interacts with the niobium center of **1a** to form Nb(IV) species **B** with a monoanionic α-diimine ligand, and then the niobium complex **B** reversibly cleaves the C—Cl bond of CCl_4 *via* a one-electron redox process to generate a dormant species **C**. In this process, one electron in the ene-diamido ligand in **1a** is effectively transferred to CCl_4 through the metal center, resulting in a change in the coordination mode of a folded ene-diamido ligand to a planar radical monoanionic ligand by the interaction of CCl_4 with the metal center. Styrene reacts with the organic radical within the coordination sphere of **C** to generate a new radical (**D**). Then, the radical abstracts a chloride atom bound to the niobium center in **D**, leading to product **4a** with regeneration of complex **1a**. Overall, the redox-active α-diimine ligand plays an important role in the redox events to form **B** and regenerate **1a** by flexibly changing the folding and planar MN_2C_2 metallacycle moiety. The large negative activation entropy value is in good accordance with the mechanism, in which **1a**, CCl_4, and styrene are involved in the transition state going from **C** to **1a**. The absence of styrene oligomers or polymers during the radical addition reaction indicated the formations of **C**[27] and **D** rather than free radicals. Scheme 2 also shows that **A** is not involved in the catalytic cycle.

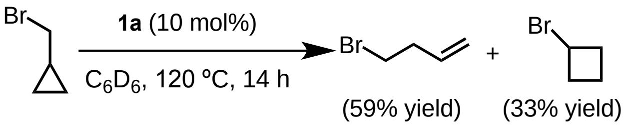
Scheme 2. Proposed reaction mechanism for radical addition reactions.



The stereoselective reaction of CCl_4 to cyclopentene provides further evidence for the inner sphere radical formation (**D**) because the *cis*/*trans* ratio of the products is dependent on the degree of freedom associated with the intermediate 2-(trichloromethyl)cyclopentyl radical. In the case of radical addition initiated by free radicals, no stereoselectivity is generally observed.[22] On the other hand, addition of CCl_3 and Cl radicals proceeded stereoselectively within the metal coordination sphere through ordered transition state **D**. Lower stereoselectivity was observed when $NbCl_3$(DME) was used as a catalyst during the reaction (Scheme 1b); however, using **1a**, the redox-active α-diimine ligand was able to support the redox events on the d^0 niobium center during the catalytic reaction, thus giving only *trans*-1-chloro-2-(trichloromethyl)cyclopentane in a selective manner (Scheme 1a).

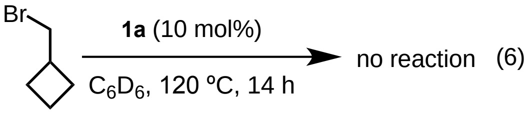
Reactivity of niobium complex 1a toward radical clock substrates

To elucidate the C—X bond activation step, we examined the reaction of **1a** with (bromomethyl)cyclopropane and (bromomethyl)cyclobutane. Treatment of (bromomethyl)cyclopropane with **1a** (10 mol%) in C_6D_6 at 120 ºC for 14 h resulted in a mixture of 4-bromobutene (59%) and bromocyclobutane (33%) along with (bromomethyl)cyclopropane (eq 5), indicating the formation of a cyclopropylmethyl radical, which is rapidly rearranged to the homoallyl radical in less than 1.1 x 10^{-8} s before reformation of a C—Br bond to give 4-bromobutene.[28] We carried out the addition of TEMPO to trap the cyclopropylmethyl radical; however, we observed only the TEMPO-induced decomposition of **1a**. Although the mechanism for the formation of bromocyclobutane in eq 5 is not clear, we postulate that cyclization to the four-membered ring proceeded through the generation of a transient homoallyl cation.[29]



(5)

In contrast to the results observed for (bromomethyl)cyclopropane, no rearrangement products were detected in the reaction of (bromomethyl)cyclobutane with **1a** (10 mol%). The cyclobutylmethyl radical is known to rearrange to the pent-4-enyl radical within 2.0 x 10^{-4} s (eq 6).[28] Thus, the C—Br bond was reversibly cleaved and formed by **1a** in the range of 5.0 x 10^3—9.4 x 10^7 s^{-1}.[28]



Oxidation of 1a by alkyl halides

As shown in Scheme 2, the catalytic cycle involves Nb(V) species bearing a monoanionic **L1** after cleavage of the C—X bond. To detect such Nb(V) species, we monitored the reaction of **1a** with excess Ph_2CCl_2 in benzene at 60 ºC by UV-vis spectroscopy (Figure 7, eq 7), as the Ph_2CCl radical derived from Ph_2CCl_2 is more stable than the CCl_3 radical. After addition of excess Ph_2CCl_2 to **1a** in benzene, a new absorption band was observed around 760 nm as well as a shoulder at 475 nm, which were both assigned to a Ph_2CCl_2-interacted species involving a planar monoanionic α-diimine ligand similar to the alkene- and CCl_4-coordinated species **A** and **B**. An additional evidence for the interaction of halogenated compounds of the halogenation interaction was the broad absorption at 748 nm for the green solution of **1a** in fluorobenzene in the same manner as **B** (Figure S16). Further heating at 60 °C resulted in the formation of a new band at 785 nm assignable to a new niobium complex. This niobium species was alternatively prepared by reducing $NbCl_5$ with 0.5 equiv. of *Si*-Me-CHD in the presence of α-diimine ligand **L1** at room temperature in toluene for 14 h, producing **6a** with a monoanionic **L1** in 59% isolated yield (eq 8), whose spectral data were superimposable with those of the detected niobium species. Accordingly, we concluded that the reductive cleavage of C—X bonds induced oxidation of **L1** in **1a** from its dianionic form to its monoanionic form, which was in sharp contrast to the metal-centered redox processes observed in previous reports of ATRP by Mo(III) complexes bearing α-diimine ligands.[30]

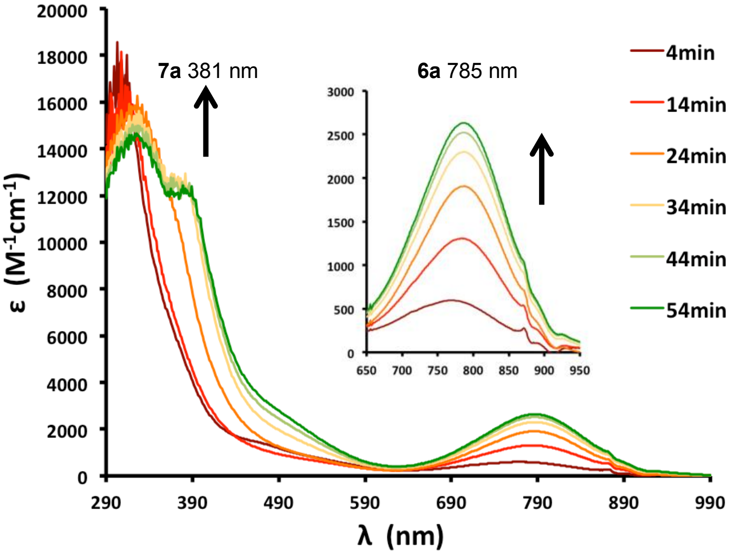
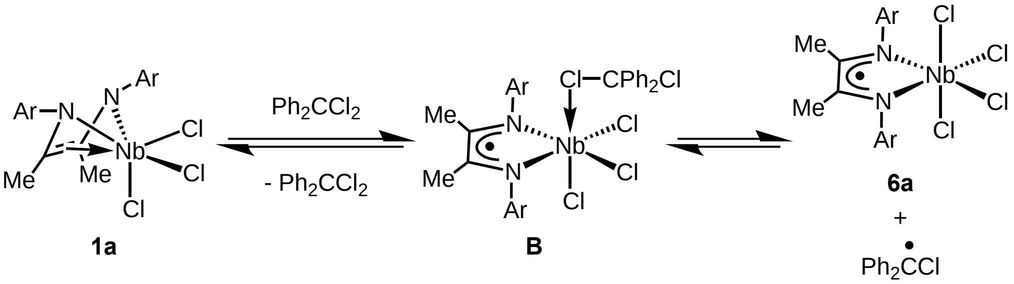
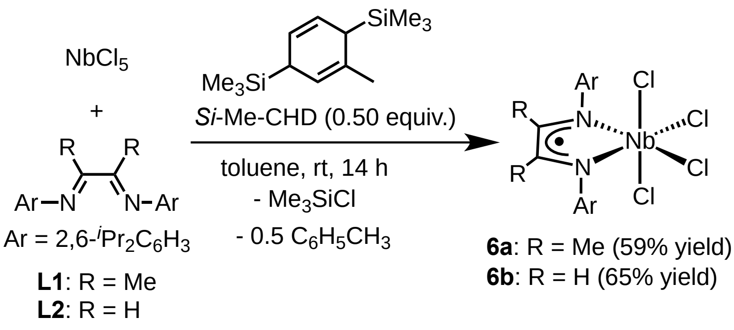


Figure 7. Time-dependent UV-vis transition for the reaction of **1a** and Ph_2CCl_2 in benzene at 60 ºC, giving **6a**, in the range of 0–60 min.



(7)



(8)

The solid-state structure of **6a** was determined by X-ray diffraction (Figure 8 and Table 4). The niobium is surrounded by four chlorides and two nitrogen atoms of the monoanoinic α-diimine ligand; the C—N and C—C bond lengths of the **L1** backbone are intermediate between those of the neutral[31] and dianionic forms of **L1**:[18b,e,i,19] the elongated C—N [1.309(17) and 1.318(17) Å] and shortened C—C [1.457(14) Å] bonds compared with the fully oxidized α-diimine form suggests the partial reduction of **L1** to the monoanionic form.[18b,e,f,h,i,20] In contrast to **1a**, the five-membered metallacycle containing **L1** and the niobium atom is planar (178.1(5)º), in good accordance with a radical anionic canonical form.[18b,e,f,h,i,20] The Nb—N distances [2.228(9) and 2.235(10) Å] are slightly longer than typical niobium-nitrogen single bonds (1.935—2.102 Å).[18b,e,f,h,i,20] The absorption maximum at 785 nm (ε = 2.5 x 10^3 M^{-1} cm^{-1}) is also consistent with a complex containing a planar metallacycle with a monoanionic α-diimine ligand.[20n,24]

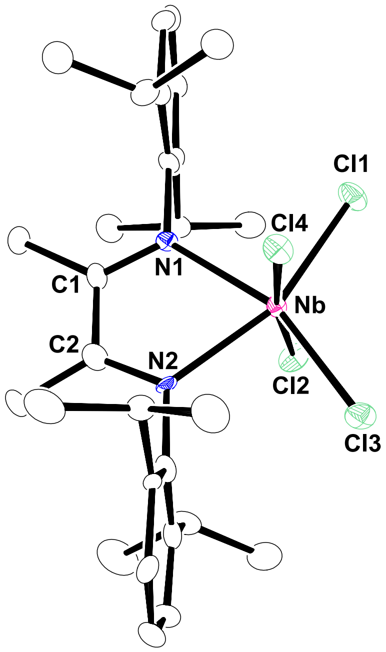


Figure 8. Molecular structure of **6a** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

Table 4. Selected bond distances (Å) and angles (deg) of **6a**.

Nb—N1	2.228(9)	N1—C1	1.309(17)
Nb—N2	2.235(10)	N2—C2	1.318(17)
Nb—Cl1	2.326(3)	C1—C2	1.457(14)
Nb—Cl2	2.386(3)	N1—Nb—N2	71.1(3)
Nb—Cl3	2.354(3)	N1—Nb1—Cl1	88.6(3)
Nb—Cl4	2.378(3)	N1—Nb1—Cl2	95.4(2)
α-diimine-fold angle[a]	178.1(5)		

[a] α-diimine-fold angle: dihedral angle between N1—C1—C2—N2 and N1—Nb—N2 planes

In addition to complex **6a**, we prepared $NbCl_4$(**L2**) (**6b**) in a similar manner (eq 8), and measured the ESR spectra of **6a** and **6b**. The ESR spectrum of **6a** displayed a ten-line splitting signal due to the 9/2 nuclear spin of ^{93}Nb (g = 1.918, A_{iso} = 105 G) (Figure 9a). The isotropic hyperfine coupling constant was lower than that of the purely localized niobium-centered radical complex, $NbCl_4(PEt_3)_2$ (A_{iso} = 141.5 G),[32] probably due to the coordination of the electron-accepting α-diimine ligand to the metal center. Although this implied that the ligand supported some of the radical character, any hyperfine coupling to the ligand only served to broaden the peaks. In contrast, the ESR spectrum for **6b** showed a nine-line with a much weaker hyperfine coupling constant consistent with an organic radical (g = 2.003, A_{iso} = 6.56 G). This was simulated by taking into account hyperfine coupling with two virtually identical nitrogen atoms (a_N = 6.80 G) and four equivalents hydrogen atoms of N=CH as well as the *para*-hydrogen atom of the *N*-aryl group (a_H = 6.31 G) (Figure 9b, c and S18).[18i] Accordingly, **6b** possessed a purely α-diimine ligand-localized radical. Different electron-accepting character of α-diimine ligands **L1** and **L2** was similarly observed for the related tantalum and tungsten complexes systems.[18i,k]

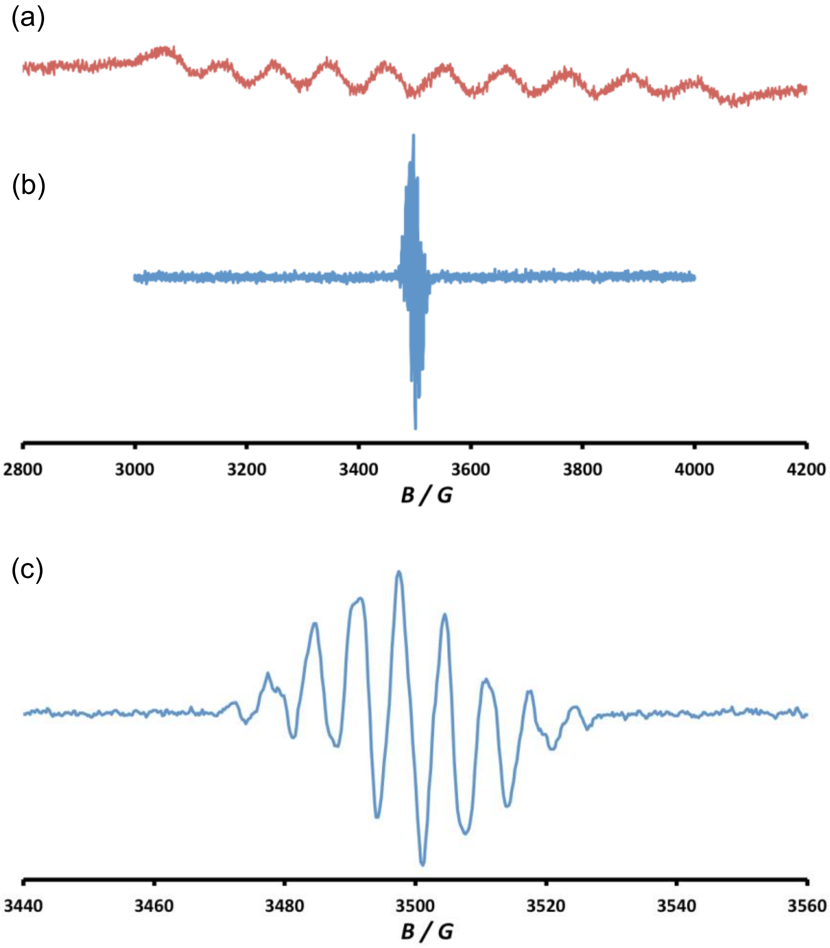


Figure 9. ESR spectra in toluene at room temperature for (a) **6a** in the range of 2800–4200 G (red line), (b) **6b** in the range of 3000–4000 G (blue line), and (c) **6b** in the range of 3440 – 3560 G (blue line).

Deactivation process to give 7a

Upon prolonged reaction of **1a** with Ph_2CCl_2 in benzene, UV-vis measurement revealed a decrease in the intensity of the absorption band at 785 nm corresponding to **6a** with an increase in the absorption at 381 nm assignable to niobium species **7a**

(Figure 10, eq 9), the product of hydrogen atom abstraction from the ligand of **6a** by a Ph_2CCl radical. Alternatively, treatment of **1a** with excess Ph_3CCl at 60 ºC in benzene for 20 h led to the formation of **7a** in 82% yield (eq 10). In the ^{1}H NMR spectrum of **7a**, two broad doublet resonances were observed at δ_H 4.44 and 4.08 corresponding to the vinylidene moiety of the ligand backbone. We previously reported a similar reaction product from the reaction of the tantalum complex **2a** with CCl_4.[18i] The $^{13}C\{^1H\}$ NMR spectrum of **7a** displayed a signal due to an imine carbon at δ_C 179.7 as well as signals due to the vinylidene carbons at δ_C 156.1 and 112.7, suggesting the formation of an enamido-imine ligand framework. In contrast, the reaction of **1a** with Ph_2CCl_2 in the presence of styrene afforded the corresponding radical addition product without any formation of **7a**, suggesting that the deactivation process for producing **7a** did not occur in the presence of alkene substrates.[33]

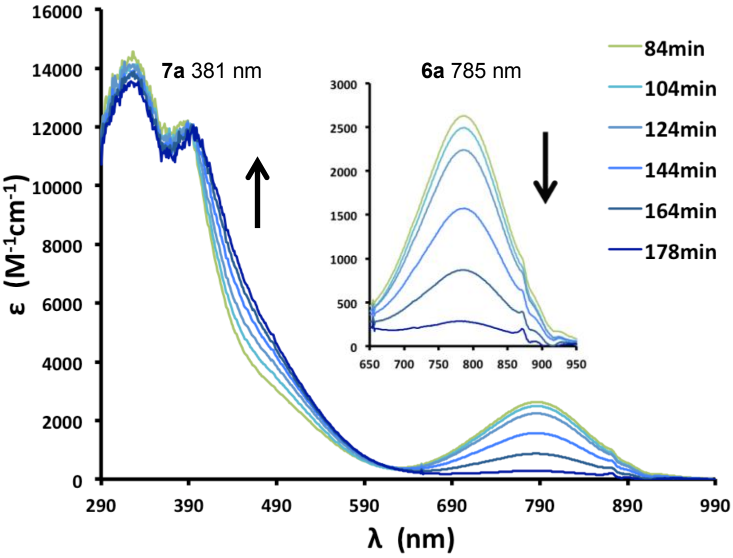
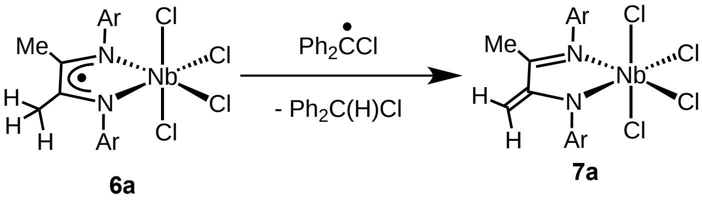
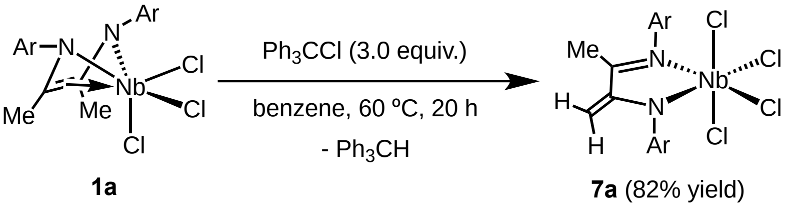


Figure 10. Time-dependent UV-vis transition for the reaction of **1a** and Ph_2CCl_2 in benzene at 60 ºC in the range of 60–180 min, corresponding to the conversion of **6a** to **7a**.


Ar
Cl
Me
N
Nb
Cl
H
H
H
N
Ar
Cl
Cl
6a
Ph2CCl
- Ph2C(H)Cl
Ar
Cl
Me
N
Nb
Cl
H
H
N
Ar
Cl
Cl
7a

(9)


N
Ar
Ar
N
Nb
Cl
Cl
Me
Me
Cl
1a
Ph3CCl (3.0 equiv.)
benzene, 60 ºC, 20 h
- Ph3CH
Ar
Cl
Me
N
Nb
Cl
H
H
N
Ar
Cl
Cl
7a (82% yield)

(10)

Conclusions

We investigated a radical addition of CCl_4 to various alkenes catalyzed by d^0 niobium complex **1a** with a redox-active α-diimine ligand. In this catalytic transformation, the α-diimine ligand played an important role in releasing and storing one electron during the C—X bond activation and re-forming steps without changing the oxidation state of the niobium center of **1a**. A key event in the electron transfer was the flexible coordination of the ene-diamido ligand: the η^4-(σ^2,π) coordination of the ene-diamido ligand stored an electron in the ligand framework while the planar κ^2-(*N*,*N'*) coordination of the ene-diamido ligand released one-electron to the niobium center. Effective overlap of the π-electrons of the dianionic ene-diamido ligand and the d-orbital of the niobium center in the planar coordination mode accelerated the one-electron transfer from the ligand to the niobium center to afford a Nb(IV) species that cleaved a C—Cl bond of CCl_4. Kinetic studies of the radical addition revealed that the reaction rate obeyed first-order kinetics with respect to the concentrations of **1a**, styrene, and CCl_4 under low concentrations of styrene and CCl_4. Organic radicals always stayed in the inner sphere of the niobium center during the catalytic reactions, which was in good agreement with the negative activation entropy and high stereoselectivity in the radical addition of CCl_4 to cyclopentene. Thus, we anticipate that the combination of a d^0 metal center with a redox-active ligand is a good candidate for controlling one-electron redox processes to mediate various catalytic radical reactions. Further studies of the catalytic application of d^0 metal complexes with redox-active ligands are ongoing in our laboratory.

Experimental Section

General Procedure

All manipulations involving air- and moisture-sensitive compounds were carried out under argon using the standard Schlenk technique or argon-filled glovebox. 1-Methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (*Si*-Me-CHD)[34], *N,N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-2,3-dimethyl-1,3-butadiene (**L1**)[35], and *N,N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (**L2**)[36] were prepared according to the literature procedures. $NbCl_3$(DME) was purchased and used as received. Anhydrous hexane, toluene, and dichloromethane were purchased from Kanto Chemical and further purified by passage through activated alumina under positive argon pressure as described by Grubbs *et al.* Alkyl halides, alkenes, *N,N,N′,N′*-tetramethylethylenediamine, and benzene were purchased and, if necessary, purified by distillation over CaH_2. Benzene-*d*$_6$, toluene-*d*$_8$, CD_3CN, and THF-*d*$_8$ were distilled over CaH_2 and degassed before use. ^{1}H NMR (400 MHz), ^{19}F{^{1}H} NMR (376 MHz), and ^{13}C{^{1}H} NMR (100 MHz) spectra were measured on BRUKER AVANCEIII-400 spectrometers and JEOL JNM-ECS400 (400 MHz) spectrometers. Assignments for ^{1}H and ^{13}C{^{1}H} NMR peaks for some of the complexes and products were aided by 2D ^{1}H—^{1}H COSY, 2D ^{1}H—^{13}C HMQC, and 2D ^{1}H—^{13}C HMBC spectra. The elemental analyses were recorded by using PerkinElmer 2400 at the Faculty of Engineering Science, Osaka University. All melting points were measured in sealed tubes under argon atmosphere on BUCHI Melting Point M-565. UV−vis spectra were recorded using an Agilent 8453 instrument. Mass spectra were obtained on and JEOL JMS-700. The ESR spectra were recorded at 298 K on a Bruker EMX-10/12 spectrometer in toluene, CH_3CN, THF, and CH_2Cl_2.

Synthesis of $NbCl_3$(L1) (1a)

A solution of **L1** (1.50 g, 3.70 mmol) and *Si*-Me-CHD (1.05 mL, 3.70 mmol) in toluene (30 mL) was added to a solution of $NbCl_5$ (1.00 g, 3.70 mmol) in toluene (30 mL) at room temperature. The color of the solution changed to deep brown. The reaction mixture was stirred for 16 h, and then all volatiles were removed under reduced pressure to give red brown solid. The precipitate was extracted with toluene (2×20 mL), and then all volatiles were removed under reduced pressure to give red solid. The solid was washed with hexane (3×10 mL). The remaining solid was dried to give **1a** as red powder in 65% yield (1.52 g, 2.52 mmol), mp 183-185 ºC (dec). ^{1}H NMR (400 MHz, C_6D_6, 303 K) δ 1.01 (d, $^3J_{HH}$ = 5.8 Hz, 12H, $CH(CH_3)_2$), 1.32 (d, $^3J_{HH}$ = 5.8 Hz, 12H, $CH(CH_3)_2$), 1.85 (s, 6H, $NC(CH_3)$), 2.85 (sept, $^3J_{HH}$ = 5.8 Hz, 4H, $CH(CH_3)_2$), 7.09—7.11 (m, 6H, aromatic protons). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 303 K) δ 15.0 ($N{=}C(CH_3)$), 24.4 ($CH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 110.8 ($NCCH_3$), 124.7 (*m*-Ar), 129.4 (*p*-Ar), 144.2 (*o*-Ar), 144.9 (*ipso*-Ar). Anal. Calcd for $C_{28}H_{40}Cl_3N_2Nb$: C, 55.69; H, 6.68; N, 4.64. Found: C, 55.91; H, 6.78; N, 4.60. λ_{max}/nm (ε/M^{-1} cm^{-1}): 464 (1.38×10^3).

Complex **1b** was prepared in similar manner as **1a**. Orange powder was obtained in 91% yield, 209-210 ºC (dec). ^{1}H NMR (400 MHz, C_6D_6, 303 K) δ 1.11 (d, $^3J_{HH}$ = 5.8 Hz, 12H, $CH(CH_3)_2$), 1.29 (d, $^3J_{HH}$ = 5.8 Hz, 12H, $CH(CH_3)_2$), 2.84 (sept, $^3J_{HH}$ = 5.8 Hz, 4H, $CH(CH_3)_2$), 5.76 (s, 2H, $N{=}CH$), 7.07—7.16 (m, 6H, aromatic protons). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 303 K) δ 24.3 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 29.0 ($CH(CH_3)_2$), 103.8 (NCH), 124.4 (*m*-Ar), 129.4 (*p*-Ar), 138.4 (*o*-Ar), 143.6 (*ipso*-Ar). Anal. Calcd for $C_{26}H_{36}Cl_3N_2Nb$: C, 54.23; H, 6.30; N, 4.86. Found: C, 54.52; H, 6.41; N, 4.84. λ_{max}/nm (ε/M^{-1} cm^{-1}): 441 (1.46×10^3), 533 (9.87×10^2), 574 (8.31×10^2).

Synthesis of $NbCl_3$(TMEDA)

A solution of *N,N,N′,N′*-tetramethylethylenediamine (66.0 μL, 0.444 mmol) and *Si*-Me-CHD (106 mg, 0.444 mmol) in CH_2Cl_2 (10 mL) was added to a solution of $NbCl_5$ (0.100 g, 0.370 mmol) in CH_2Cl_2 (10 mL) at 0 ºC. The color of the solution changed to pink. The reaction mixture was stirred for 20 h at room temperature, and then all volatiles were removed under reduced pressure to give pink solid. The precipitate was washed with hexane (3 × 2 mL). The remaining solid was dried to give $NbCl_3$(TMEDA) as red powder in 75% yield (86.7 mg, 0.276 mmol), mp 179-180 ºC (dec). ^1H NMR (400 MHz, CD_2Cl_2, 303 K) δ 1.31 (s, 12H, $N(CH_3)_2$), 2.45 (s, 4H, CH_2N). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 303 K) δ 54.5 (CH_2N), 58.6 ($N(CH_3)_2$). Anal. Calcd for $C_6H_{16}Cl_3N_2Nb$: C, 22.84; H, 5.11; N, 8.88. Found: C, 23.15; H, 4.85; N, 8.58.

Synthesis of $NbCl_4$(L1) (6a)

Si-Me-CHD (0.120 mL, 0.425 mmol) was added to a solution of $NbCl_5$ (230 mg, 0.850 mmol) in toluene (10 mL). Then, a solution of **L1** (343 mg, 0.850 mmol) in toluene (10 mL) was added to reaction mixture at room temperature. The color of the solution changed to green. The reaction mixture was stirred for 14 h, and then volatiles were removed under reduced pressure to give a green solid. The solid was extracted with CH_2Cl_2 (20 mL) and washed with toluene (3 × 10 mL) and hexane (3 × 10 mL), and then dried to give **6a** as green powder in 59% yield (319 mg, 0.498 mmol), mp 169-170 ºC (dec). ESR (toluene): $g = 1.918$, ($A_{iso} = 105$ G). Anal. Calcd for $C_{28}H_{40}Cl_4N_2Nb$; C, 52.60; H, 6.31; N, 4.38. Found: C, 52.43; H, 4.60; N, 4.36. λ_{max}/nm (ε/M^{-1} cm^{-1}): 785 (2.53×10^3).

Complex **6b** was prepared in similar manner as **6a**. Green powder was obtained in 65% yield, mp 165-167 ºC (dec). ESR (toluene): g = 2.003 (A_{iso} = 6.56 G). Anal. Calcd for $C_{26}H_{36}Cl_4N_2Nb$; C, 51.08; H, 5.94; N, 4.58. Found: C, 51.52; H, 5.76; N, 4.58. λ_{max}/nm (ε/M^{-1} cm^{-1}): 814 (1.17x 10^3).

Synthesis of $NbCl_4$(enamido-imino) (7a)

A solution of Ph_3CCl (144 mg, 0.500 mmol) in benzene (10 mL) was added to a solution of complex **1a** (100 mg, 0.166 mmol) in benzene (10 mL) at room temperature. The reaction mixture was stirred for 20 h at 60 ºC, and then all volatiles were removed under reduced pressure to give green solid. The solid was washed with hexane (3 × 10 mL) and dried to give **7a** as lime green powder in 82% yield (87.0 mg, 0.136 mmol), mp 115-116 ºC (dec). ^{1}H NMR (400 MHz, C_6D_6, 303 K) δ 0.93 (d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.03 (d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.47 (s, 3H, NC(CH_3)), 1.50 (d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.53 (d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 6H, CH(CH_3)$_2$), 3.27 (sept, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 3.75 (sept, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 4.08 (brd, ^{1}H, NC=CH_2), 4.44 (brd, ^{1}H, NC=CH_2), 7.0—7.4 (m, 6H, aromatic protons). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 303 K) δ 19.1 (N=C(CH$_3$)), 24.1 (CH(CH$_3$)$_2$), 25.2 (CH(CH$_3$)$_2$), 25.2 (CH(CH$_3$)$_2$), 26.9 (CH(CH$_3$)$_2$), 29.0 (CH(CH$_3$)$_2$), 29.6 (CH(CH$_3$)$_2$), 112.7 (N=C=CH$_2$), 124.9 (*m*-Ar), 126.2 (*m*-Ar), 125.8 (Ar), 127.9 (Ar), 128.8 (Ar), 131.2 (*o*-Ar), 140.8 (Ar), 145.2 (*o*-Ar), 156.1 (N=C=CH$_2$), 179.7 (C=N). Anal. Calcd for $C_{28}H_{39}Cl_4N_2Nb$: C, 52.68; H, 6.16; N, 4.39. Found: C, 52.84; H, 5.91; N, 4.13. λ_{max}/nm (ε/M^{-1} cm^{-1}): 381 (4.96 x 10^3).

General Procedure for Catalytic Radical Addition Reaction (Tables 2, 3, and Scheme 1)

To a pre-mixed solution of alkyl halide (1.50 mmol), alkene (0.300 mmol), and 1,4-dioxane (55.0 mg, 0.300 mmol) as an internal standard in the reaction solvent (0.3 mL) was added metal catalyst placed (9.00 μmol) in a J-Young NMR tube. The NMR sample of the reaction mixture was kept in oil bath (100 ºC). After the appropriate reaction time, the sample was measured by ^{1}H NMR.

General Procedure for Product Isolation of Radical Addition Reaction catalyzed Complex 1a (Tables 2 and 3)

To a solution of alkyl halide (15.0 mmol) and alkene (3.00 mmol) in benzene (2.0 mL) was added to **1a** (0.0900 mmol) in a vial. The vial was capped with a PTFE-lined cap, and heated to 100 ºC by aluminum block bath. The reaction mixture was quenched by exposing to air after the reaction time, and all the volatiles were removed by evacuation. The reaction mixture was concentrated and purified by Kugelrohr distillation. After the reaction, the mixture was measured by ^{1}H and ^{13}C{^{1}H} NMR.

Kinetic Study of the Radical Addition Reaction of CCl_4 to Styrene at Different Catalyst Concentration

In a glovebox under argon, complex **1a** (18, 30, 36, 42, 60, and 72 mM), styrene (0.60 M), CCl_4 (3.0 M), and hexamethylbenzene (0.60 M) as an internal standard were dissolved in the required amount of C_6D_6 to complete a total volume of 0.5 mL. The solutions were transferred to into six J-Young NMR tubes. The tubes were kept at 100 ºC in the JEOL JNM-ECS400. The yield of the product was determined by integral ratios of ^{1}H NMR signals of hexamethylbenzene and PhC*H*ClCH$_2$CCl$_3$.

Kinetic Study of the Radical Addition Reaction of CCl$_4$ to Styrene at Different Styrene Concentration

In a glovebox under argon, complex **1a** (18 mM), styrene (0.20, 0.30, 0.40, 0.60, 0.90, 1.2, 1.5, and 1.8 M), CCl$_4$ (4.5 M), and hexamethylbenzene (0.60 M) as an internal standard were dissolved in the required amount of C$_6$D$_6$ to complete a total volume of 1.0 mL. The solutions were transferred to into eight J-Young NMR tubes. The tubes were kept at 100 ºC in the JEOL JNM-ECS400. The yield of the product was determined by integral ratios of ^{1}H NMR signals of hexamethylbenzene and PhC*H*ClCH$_2$CCl$_3$.

Kinetic Study of the Radical Addition Reaction of CCl$_4$ to Styrene at Different CCl$_4$ Concentration

In a glovebox under argon, complex **1a** (18 mM), styrene (0.60 M), CCl$_4$ (2.4, 3.0, 3.6, 4.2, 4.8, 5.4, 6.0 and 6.6 M), and hexamethylbenzene (0.60 M) as an internal standard were dissolved in the required amount of C$_6$D$_6$ to complete a total volume of 0.5 mL. The solutions were transferred to into eight J-Young NMR tubes. The tubes were kept at 100 ºC in the JEOL JNM-ECS400. The yield of the product was determined by integral ratios of ^{1}H NMR signals of hexamethylbenzene and PhC*H*ClCH$_2$CCl$_3$.

Kinetic Study of the Radical Addition Reaction of CCl$_4$ to Styrene at Different Temperature

In a glovebox under argon, complex **1a** (18 mM), styrene (0.60 M), CCl$_4$ (3.0 M), and hexamethylbenzene (0.60 M) as an internal standard were dissolved in the required amount of C_6D_6 to complete a total volume of 0.5 mL. The solutions were t transferred to five J-Young NMR tubes. The temperature was controlled in the range of 73-92 ºC in the JEOL JNM-ECS400. The yield of the product was determined by integral ratios of ^{1}H NMR signals of hexamethylbenzene and $PhC\mathit{H}ClCH_2CCl_3$.

Reaction of 1a with (Bromomethyl)cycloalkane

To a solution of (bromometyl)cycloalkane (0.300 mmol) and 1,4-dioxane (55.0 mg, 0.300 mmol) as internal standard in C_6D_6 (0.5 mL) was added to **1a** (30.0 μmol) in J-Young NMR tube. The NMR sample of this mixture was kept in oil bath (120 ºC) for 14 h. After the reaction, the mixture was measured by ^{1}H NMR.

Time-dependent UV-vis Spectra

A 1.0 cm UV cell containing 0.414 mM of **1a** and 1.24 mM of Ph_2CCl_2 was placed in a UV-vis spectrophotometer. The UV cell was heated at 60 ºC for 3 h under argon, and the progress of the reaction was monitored at intervals of 4 min by UV-vis spectrophotometry (Figures 7 and 10).

X-ray Diffraction Study

Crystals were mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(1) K. Measurements were made on Rigaku R-AXIS RAPID imaging plate area detector Rigaku AFC7R/Mercury CCD detector with graphite-monochromated Mo Kα (0.71075 Å) radiation. Crystal data and structure refinement parameters are listed in Table S1.

The structures of complexes **1a**,**b**, **5b** and **6a** were solved by SIR-92.[37] The structure of complex **6b** was solved by SHELX-97.[38] The structures were refined on F^2 by full-matrix least-squares method, using SHELXL-97.[38] Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (a\mathrm{P})^2 + b\mathrm{P}]$), where $P = (\mathrm{Max}(F_o^2,0) + 2\mathrm{F}_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions $R1$ and $wR2$ were $(\sum||F_o| - |F_c||)/\sum|F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum(w\ F_o^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecules.[39]

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Supporting Information

Experimental details, molecular structure of **1b**, **5b** and **6b**, VT-NMR measurement of **1a**, kinetic study, synthesis of complexes **5a** and **5b**, UV-vis spectra of **1a, 5a, 6a** and **7a**, ESR spectra of **6a** and **6b**, NMR spectra of products, crystal data and data collection parameters, and CIF file giving data for complexes **1a**, **1b**, **5b**, **6a**, and **6b**. This material is available free of charge *via* the Internet at http://pubs.acs.org.

References and Notes

(1) Representative books for radical reactions in organic chemistry: (a) Giese, B. *Radicals in organic synthesis: Formation of carbon—carbon bonds*; Pergamon Press: Oxford, 1986. (b) Fossey, J.; Lefort, D.; Sorba. J. *Free Radicals in Organic Chemistry*; Wiley: Weinheim, 1995. (c) Zard. S. Z. *Radical Reaction in Organic Synthesis*; Oxford University Press: Oxford, 2004. (d) *Radicals in Synthesis I*; Gansäuer, A. Ed; Springer: Heidelberg, 2006. (e) *Radicals in Synthesis II*; Gansäuer, A. Ed; Springer: Heidelberg, 2006. (f) *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P. Eds.; Wiley: Weinheim, 2008. (g) *Radicals in Synthesis III*; Heinrich, M. R., Gansäuer, A. Eds; Springer: Heidelberg, 2012.

(2) Denisov, E. T.; Denisova, T. G.; Pokidova, T. S. *Handbook of Free Radical Initiatoes*; Wiley: Weinheim, 2003.

(3) (a) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *Science* **1945**, *102*, 128. (b) Kharasch, M. S.; Skell, P. S.; Fischer, P. *J. Am. Chem. Soc.* **1948**, *70*, 1055.

(4) Representative reviews for metal-catalyzed radical addition reaction: (a) Minisci, F. *Acc. Chem. Res*. **1975**, *8*, 165. (b) Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem. Rev.* **1994**, *94*, 519. (c) Gossage, R. A.; van de Kuil, L. A.; van Koten, G. *Acc. Chem. Res*. **1998**, *31*, 423. (d) Clark, A. J. *Chem. Soc. Rev*. **2002**, *31*, 1. (e) Delaude, L.; Demonceau, A.; Noels, A. F. *Top. Organomet. Chem.* **2004**, *11*, 155. (f) Severin, K. *Curr. Org. Chem*. **2006**, *10*, 217. (g) Pintauer, T.; Matyjaszewski, K. *Chem. Soc. Rev.* **2008**, *37*, 1087. (h) Eckenhoff, W. T.; Pintauer, T. *Catal. Rev.* **2010**, *52*, 1. (i) Pintauer, T. *Eur. J. Inorg. Chem.* **2010**, 2449.

(5) Representative examples for the radical addition reaction by Ru catalyst: (a) Tallarico, J. A.; Malnick, L. M.; Snapper, M. L. *J. Org. Chem*. **1999**, *64*, 344. (b)

Simal, F.; Wlodarczak, L.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **2000**, *41*, 6071. (c) Tutusaus, O.; Viñas, C.; Núñez, R.; Teixidor, F.; Demonceau, A.; Delfosse, S.; Noels, A. F.; Mata, I.; Molins, E. *J. Am. Chem. Soc.* **2003**, *125*, 11830. (d) De Clercq, B.; Verpoort, F. *J. Organomet. Chem.* **2003**, *672*, 11. (e) Tutusaus, O.; Delfosse, S.; Demonceau, A.; Noels, A. F.; Viñas, C.; Teixidor, F. *Tetrahedron Lett.* **2003**, *44*, 8421. (f) Quebatte, L.; Scopelliti, R.; Severin, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1520. (g) Lundgren, R. J.; Rankin, M. A.; McDonald, R.; Stradiotto, M. *Organometallics* **2008**, *27*, 254. (h) Lee, J.; Grandner, J. M.; Engle, K. M.; Houk, K. N.; Grubbs, R. H. *J. Am. Chem. Soc.* **2016**, *138*, 7171.

(6) Representative examples for the radical addition reaction by Fe catalyst: (a) De Malde, M.; Minisci, F.; Pallini, U.; Volterra, E.; Quilico, A. *Chim. Ind.* **1956**, *38*, 371. (b) Minisci, F.; Galli, R. *Chim. Ind.* **1963**, *45*, 1400. (c) Forti, L.; Ghelfi, F.; Pagnoni, U. M. *Tetrahedron Lett.* **1996**, *37*, 2077. (d) Forti, L.; Ghelfi, F.; Libertini, E.; Pagnoni, U. M.; Soragni, E. *Tetrahedron Lett.* **1997**, *53*, 17761. (e) Eckenhoff, W. T.; Biernesser, A. B.; Pintauer, T. *Inorg. Chim. Acta* **2012**, *382*, 84.

(7) Representative examples for the radical addition reaction by Ni catalyst: (a) van de Kuil, L. A.; Grove, D. M.; Gossage, R. A.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1997**, *16*, 4985. (b) Kleij, A. W.; Gossage, R. A.; Klein Gebbink, R. J. M.; Brinkmann, N.; Reijerse, E. J.; Kragl, U.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc*. **2000**, *122*, 12112. (c) Pandarus, V.; Zargarian, D. *Chem. Commun.* **2007**, 978.

(8) Representative examples for the radical addition reaction by Cu catalyst: (a) Hajek, M.; Silhavy, P. *Collect. Czech. Chem. Commun.* **1980**, *48*, 1710. (b) Kotora, M.; Hajek, M. *J. Mol. Catal. A* **1992**, *77*, 51. (c) Villemin, D.; Sauvaget, F.; Hajek, M.

Tetrahedron Lett. **1994**, *35*, 3537. (d) Davies, R.; Stephens, K.; Hajek, M. J. *Mol. Catal. A* **1994**, *92*, 269. (e) Nicole, M.; Pintauer, T. *Inorg. Chem.* **2009**, *48*, 9018. (f) Muñoz-Molina, J. M.; Belderraín, T. R.; Pérez, P. J. *Inorg. Chem.* **2010**, *49*, 642. (g) Muñoz-Molina, J. M.; Sameera, W. M.; Álvarez, E.; aseras, F.; Belderraín, T. R.; Pérez, P. J. *Inorg. Chem.* **2011**, *50*, 2458. (h) Kamijo, S.; Yokosaka, S.; Inoue, M. *Tetrahedron Lett.* **2012**, *53*, 4324. (i) Kaur, A.; Gorse, E. E.; Ribeli, T. G.; Jerman, C. C.; Pintauer, T. *Polymer* **2015**, *72*, 246. (j) Zhao, B.; Lu, J.; Li, Y.; Tu, D.; Liu, Z.; Liu, Z.; Lu, J. *RSC. Ads.* **2015**, *5*, 10412. (k) Rexit, A. A.; Hu, X. *Tetrahedron* **2015**, *71*, 2313. (l) Li, G.; Cao, Y.; Luo, C.; Su, Y.; Li, Y.; Lan, Q.; Wang, X. *Org. Lett.* **2016**, *18*, 4806.

(9) Representative examples for the radical addition reaction by Cu catalyst with reductant: (a) Eckenhoff, W. T.; Pintauer, T. *Inorg. Chem.* **2007**, *46*, 5844. (b) Eckenhoff, W. T.; Garrity, S. T.; Pintauer, T. *Eur. J. Inorg. Chem.* **2008**, 563. (c) Pintauer, T. *ACS Symp. Ser.* **2009**, *1023*, 63. (d) Pintauer, T.; Eckenhoff, W. T.; Ricardo, C.; Balili, M. N. C.; Biernesser, A. B.; Noonan, S. J.; Taylor, M. J. W. *Chem. Eur. J.* **2009**, *15*, 38. (e) Pintauer, T.; Matyjaszewski, K. *Top. Organomet. Chem.* **2009**, *26*, 221. (f) Ricardo, C.; Pintauer, T. *Chem. Commun.* **2009**, 3029. (g) Balili, M. N. C.; Pintauer, T. *Inorg. Chem.* **2010**, *49*, 5642. (h) Eckenhoff, W. T.; Pintauer, T. *Catal. Rev. Sci. Eng.* **2010**, *52*, 1. (i) Tatlor, M. J.; Eckenhoff, W. T.; Pintauer, T. *Dalton Trans.* **2010**, *39*, 11475.

(10) Representative examples for the radical addition reaction by Ru catalyst with reductant: (a) Quebatte, L.; Thommes, K.; Severin, K. *J. Am. Chem. Soc.* **2006**, *128*, 7440. (b) Thommes, K.; Icli, B.; Scopelliti, R.; Severin, K. *Chem. Eur. J.* **2007**, *13*, 6899. (c) Fernández-Zúmel, M. A.; Thommes, K.; Kiefer, G.; Sienkiewicz, A.;

Pierzchala, K.; Severin, K. *Chem. Eur. J.* **2009**, *15*, 11601. (d) Nair, R. P.; Kim, T. H.; Frost, B. J. *Organometallics* **2009**, *28*, 4681. (e) Nair, R. P.; Pineda-Lanorio, J. A.; Frost, B. J. *Inorg. Chim. Acta* **2012**, *380*, 96.

(11) Representative examples for the radical addition reaction by early transition metal catalysts: (a) Melorose, J.; Perroy, R.; Careas, S. *J. Org. Chem.* **1970**, *35*, 2982. (b) Davis, R.; Groves, I. F. *J. Organomet. Chem.* **1981**, *215*, C23. (c) Davis, R.; Groves, I. F. *J. Chem. Soc., Dalton Trans.* **1982**, 2281. (d) Bland, W. J.; Davis, R.; Durrant, J. L. A. *J. Organomet. Chem.* **1985**, *280*, 95. (e) Pereira, S.; Srebnik, M. *J. Am. Chem. Soc.* **1996**, *118*, 909. (f) Davis, R.; Khazal, N. M. S.; Bitterwolf, T. E. *J. Organomet. Chem.* **1990**, *397*, 51. (g) Hirao, T.; Ohshiro, Y.; *Synlett* **1990**, 217. (h) Shvo, Y.; Green, R. *J. Organomet. Chem.* **2003**, *675*, 77. (i) Szyma, T. *Curr. Org. Chem.* **2012**, *16*, 3.

(12) Recent examples for the radical addition reaction by photoredox catalyst: (a) Nguyen, J. D.; Tucker, J. W.; Konieczynska, M. D.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2011**, *133*, 4160. (b) Wallentin, C. -J.; Nguyen, J. D.; Finkbeiner, P.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2012**, *134*, 8875. (c) Pirtsch, M.; Paria, S.; Matsuno, T.; Isobe, H.; Reiser, O. *Chem. Eur. J.* **2012**, *18*, 7336. (d) Paria, S.; Pirtsch, M.; Kais, V.; Reiser, O. *Synthesis* **2013**, *45*, 2689. (e) Arceo, E.; Montroni, E.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2014**, *53*, 12064. (f) Tang, X.; Dolbier, Jr. W. R. *Angew. Chem., Int. Ed.* **2015**, *54*, 4246. (g) Riente, P.; Pericás, M. A. *ChemSusChem* **2015**, *8*, 1841.

(13) Representative books and reviews for ATRP: (a) Matyjaszewski, K.; Xia, J. *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P. Eds; Wiley: Weinheim, 2003. (b) Matyjaszewski, K. *Controlled and Living Polymerizations:*

From Mechanism to Applications; Müller, A. H. E., Matyjaszewski, K. Eds; Wiley: Weinheim, 2010. (c) Matyjaszewski, K. *Chem. Eur. J.* **1999**, *5*, 3095. (d) Matyjaszewski, K., Xia, J. *Chem. Rev.* **2001**, *101*, 2921. (e) Matyjaszewski, K. *Curr. Org. Chem.* **2002**, *6*, 67. (f) Braunecker, W. A.; Matyjaszewski, K. *J. Molecular Cat. A* **2006**, *254*, 155. (g) Tsarevsky, N. V.; Matyjaszewski, K. *Chem. Rev.* **2007**, *107*, 2270. (h) Poli, R.; Allan, L. E.N.; Shaver, M. P. *Prog. Poly. Sci.* **2014**, *39*, 1827.

(14) Representative reviews for transition metal complexes with redox-active ligands: (a) Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187. (b) Chirik, P. J.; Wieghardt, K. *Science* **2010**, *327*, 794. (c) Kaim, W.; Schwederski, B. *Coord. Chem. Rev*. **2010**, *254*, 1580. (d) Lyaskovskyy, V.; de Bruin, B. *ACS Catal.* **2012**, *2*, 270. (e) Praneeth, V. K. K.; Ringenberg, M. R.; Ward, T. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 10228. (f) Luca, O. R.; Crabtree, R. H. *Chem. Soc. Rev*. **2013**, *42*, 1440.

(15) Representative examples for the catalytic application of transition metal complexes with redox-active ligands: For Fe, (a) Bouwkamp, M. W.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13340. (b) Sylvester, K. T.; Chirik, P. J. *J. Am. Chem. Soc*. **2009**, *131*, 8772. (c) Russell, S. K.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc*. **2011**, *133*, 8858. (d) Hoyt, J. M.; Schmidt, V. A.; Tondreau, A. M.; Chirik, P. J. *Science* **2015**, *349*, 960. For Co, (e) Obligacion, J. V.; Neely, J. M.; Yazdani, A. N.; Pappas, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2015**, *137*, 5855. (f) Schmidt, V. A.; Hoyt, J. M.; Margulieux, G. W.; Chirik, P. J. *J. Am. Chem. Soc*. **2015**, *137*, 7903. (g) Goswami, M.; Lyaskovskyy, V.; Domingos, S. R.; Buma, W. J.; Woutersen, S.; Troeppner, O.; Ivanovic-Burmazovic, I.; Lu, H.; Cui, X.; Zhang, X. P.; Reijerse, E. J.; DeBeer, S.; van Schooneveld, M. M.; Pfaff, F. F.; Ray, K.; de Bruin, B. *J. Am. Chem. Soc.* **2015**, *137*, 5468. For Pd, (h) Broere, D. L.

J.; Demeshko, S.; de Bruin, B.; Pidko, E. A.; Reek, J. N. H.; Siegler, M. A.; Lutz, M.; van der Vlugt, J. I. *Chem. Eur. J.* **2015**, *21*, 5879. (i) Broere, D. L. J.; Metz, L. L.; de Bruin, B.; Reek, J. N. H.; Siegler, M. A.; van der Vlugt, J. I. *Angew. Chem., Int. Ed.* **2015**, *54*, 1516.

(16) Recent reviews for early transition metal complexes with redox-active ligands: (a) Munha, R. F.; Zarkesh, R. A.; Heyduk, A. F. *Dalton Trans.* **2013**, *42*, 3751. (b) O'Reilly, M. E.; Veige, A. S. *Chem. Soc. Rev.* **2014**, *43*, 6325.

(17) Recent examples for early transition metal complexes with redox-active ligands: (a) Stanciu, C.; Jones, M. E.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 12400. (b) Blackmore, K. J.; Lal, N.; Ziller, J. W.; Heyduk, A. F. *J. Am. Chem. Soc.* **2008**, *130*, 2728. (c) Zarkesh, R. A.; Ziller, J. W.; Heyduk, A. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 4715. (d) Blackmore, K. J.; Sly, M. B.; Haneline, M. R.; Ziller, J. W.; Heyduk, A. F. *Inorg. Chem.* **2008**, *47*, 10522. (e) Zarkesh, R. A. Heyduk, A. F. *Organometallics* **2011,** *30*, 4890. (f) Nguyen, A. I.; Zarkesh, R. A.; Lacy, D. C.; Thorson, M. K.; Heyduk, A. F. *Chem. Sci.* **2011**, *2*, 166. (g) Heyduk, A. F.; Zarkesh, R. A.; Nguyen, A. I. *Inorg. Chem.* **2011**, *50*, 9849. (h) Lu, F.; Zarkesh, R. A.; Heyduk, A. F. *Eur. J. Inorg. Chem*. **2012**, 467. (i) Munhá, R. F.; Zarkesh, R. A.; Heyduk, A. F. *Inorg. Chem.* **2013**, *52*, 11244. (j) Hananouchi, S.; Krull, B. T.; Ziller, J. W.; Furche, F.; Heyduk, A. F. *Dalton Trans.* **2014**, *43*, 17991.

(18) (a) Mashima, K.; Matsuo, Y.; Tani, K. *Chem. Lett.* **1997**, 767. (b) Mashima, K.; Matsuo, Y.; Tani, K. *Organometallics* **1999**, *18,* 1471. (c) Matsuo, Y.; Mashima, K.; Tani, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 960. (d) Nakamura, A.; Mashima, K. *J. Organomet. Chem.* **2001**, *621*, 224. (e) Tsurugi, H.; Ohno, T.; Kanayama, T.; Arteage-Müller, R. A.; Mashima, K. *Organometallics* **2009**, *28*, 1950. (f) Panda, T.

K.; Kaneko, H.; Pal, K.; Tsurugi, H.; Mashima, K. *Organometallics* **2010**, *29*, 2610. (g) Kaneko, H.; Nagae, H.; Tsurugi, H.; Mashima, K.; *J. Am. Chem. Soc.* **2011**, *133*, 19626. (h) Panda, T. K.; Kaneko, H.; Michel, O.; Pal, K.; Tsurugi, H.; Törnroos, K.; Anwander, R.; Mashima, K. *Organometallics* **2012**, *31*, 3178. (i) Tsurugi, H.; Saito, T.; Tanahashi, H.; Arnold, J.; Mashima, K. *J. Am. Chem. Soc.* **2011**, *133*, 18673. (j) Tanahashi, H.; Tsurugi, H.; Kazushi, M. *Organometallics* **2015**, *34*, 731. (k) Tanahashi, H.; Ikeda, H.; Tsurugi, H.; Kazushi, M. *Inorg. Chem.* **2016**, *55*, 1466.

(19) (a) Kawaguchi, H.; Yamamoto, Y.; Asaoka, K.; Tatsumi, K. *Organometallics* **1998**, *17*, 4380. (c) Scholz, J.; Habi, G. A.; Thiele, K.; Görls, H.; Weimann, R.; Schumann, H.; Sieler, J. *J. Organomet. Chem.* **2001**, *626*, 243. (d) Scholz, J.; Görls, H. *Polyhedron* **2002**, *21*, 305.

(20) (a) Herebian, D.; Bothe, E.; Neese, F.; Weyhermüller, T.; Wieghard, K. *J. Am. Chem. Soc.* **2003**, *125*, 9116. (b) Trifonov, A. A.; Fedorova, E. A.; Ikorskii, V. N.; Dechert, S.; Schumann, H.; Bochkarev, M. N. *Eur. J. Inorg. Chem.* **2005**, 2812. (c) Moore, J. A.; Cowley, A. H.; Gordon, J. C. *Organometallics* **2006**, *25*, 5207. (d) Muresan, N.; Weyhermüller, T.; Wieghardt, K. *Dalton Trans.* **2007**, 4390. (e) Muresan, N.; Chiopek, K.; Weyhermüller, T.; Neese, F.; Wieghardt, K. *Inorg. Chem.* **2007**, *46*, 5327. (f) Cui, P.; Chen, Y.; Wang, G.; Li, G.; Xia, W. *Organometallics* **2008**, *27*, 4013. (g) Ghosh, M.; Sproules, S.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2008**, *47*, 5963. (h) Muresan, N.; Lu, C. C.; Ghosh, M.; Peters, J. C.; Abe, M.; Henling, L. M.; Weyhermüller, T.; Bill, E.; Wieghardt, K. *Inorg. Chem.* **2008**, *47*, 4579. (i) Ghosh, M.; Weyhermüller, T.; Wieghardt, K. *Dalton Trans.* **2008**, 5149. (j) Kreisel, K. A.; Yap, G. P. A.; Theopold, K. H. *Inorg. Chem.* **2008**, *47*, 5293. (k) Kreisel, K. A.; Yap, G. P. A.; Theopold, K. H. *Inorg.*

Chem. **2008**, *47*, 5293. (l) Fedushkin, I. L.; Makarov, V. M.; Sokolov, V. G.; Fukin, G. K. *Dalton Trans.* **2009**, 8047. (m) Khusniyarov, M. M.; Weyhermüller, T.; Bill, E.; Wieghardt, K. *J. Am. Chem. Soc.* **2009**, *131*, 1208. (n) Zhou, W.; Chiang, L.; Patrick, B. O.; Storr, T.; Smith, K. M. *Dalton Trans.* **2012**, *41*, 5149. (o) Zhao, Y.; Liu, Y.; Yang, L.; Yu, J.; Li, S.; Wu, B.; yang, X. *Chem. Eur. J.* **2012**, *18*, 6022. (p) Li, J.; Zhang, K.; Huang, H.; Yu, A.; Cui, H.; Cui, C. *Organometallics* **2013**, *32*, 1630. (q) Yang, X.; Fan, X.; Zhao, Y.; Wang, X.; Liu, B.; Su, J.; Dong, Q.; Xu, M.; Wu, B. *Organometallics* **2013**, *32*, 6945.

(21) (a) Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901. (b) Bart, S. C.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 7212. (c) Bart, S. C.; Lobkovsky, E.; Bill, E.; Wieghardt, K.; Chirik, P. J. *Inorg. Chem.* **2007**, *46*, 7055. (d) Trovitch, R. J.; Bill, E.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2008**, *27*, 1470. (e) Steiman, T. J.; Uyeda, C. *J. Am. Chem. Soc.* **2015**, *137*, 6104.

(22) (a) Israelashvili, S.; Shabatay, J. *J. Chem. Soc.* **1951**, 3261. (b) Matsumoto, H.; Nikaido, T.; Nagai, Y. *Tetrahedron Lett.* **1975**, *11*, 899. (c) Grigg, R.; Devlin, J.; Ramasubbu, A.; Scott, R. M.; Stevenson, P. *J. Chem. Soc., Perkin Trans. I* **1987**, 1515.

(23) See content 3 in the Supporting Information.

(24) (a) Lu, C. C.; Bill, E.; Weyhermüller, Bothe, E.; Wieghard, K. *J. Am. Chem. Soc.* **2008**, *130*, 3181. (b) Myers, T. W.; Kazem, N.; Stoll, S.; Britt, R. D.; Shanmugam, M.; Berben, L. A. *J. Am. Chem. Soc.* **2011**, *133*, 8662. (c) Myers, T. W.; Berben, L. A. *J. Am. Chem. Soc.* **2011**, *133*, 11865. (d) Myers, T. W.; Berben, L. A. *Inorg. Chem.* **2012**, *51*, 1480.

(25) The reaction of **1a** (5.40 mg, 9.00 mM) and styrene (102 μL, 1.80 M) were mixed in C_6D_6 at 100 ºC for 4 h to afford the brown suspension. The ^{1}H NMR spectrum displayed peaks for a free α-diimine ligand.

(26) See content 3 in the Supporting Information.

(27) (a) Matumoto, H.; Nakao, T.; Takasu, K.; Nagai, Y. *J. Org. Chem.* **1978**, *43*, 1734. (b) Nondek, L.; Hun, L. -G.; Wichterlová, B.; Krupicka, S. *J. Mol. Catal.* **1987**, *42*, 51. (c) Davis, R.; Furze, J. D. *J. Organomet. Chem.* **1992**, *440*, 191. (d) Gossage, R. A.; Van de kuil, L. A.; van Koten, G., *Acc. Chem. Res.* **1998**, *31*, 423. (e) Caballero, A.; Díaz-Requejo, M. M.; Trofimenko, S.; Belderraín, T. R.; Pérez, P. J. *Inorg. Chem.* **2007**, *46*, 7725.

(28) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

(29) (a) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 454-463. (b) Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J. *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. 3, pp 1295-1346. (c) Schleyer, P. v. R.; Maerker, C.; Buzek, P.; Sieber, S. *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. Eds.; John Wiley and Sons: New York, 1997; pp 19-74.

(30) (a) Stoffelbach, F.; Poli, R.; Richard, P. *J. Organomet. Chem.* **2002**, *663*, 269. (b) Stoffelbach, F.; Haddleton, D. M.; Poli, R. *Eur. Polym. J.* **2003**, *39*, 2099. (c) Stoffelbach, F.; Poli, R. *Chem. Commun.* **2004**, 2666. (d) Stoffelbach, F.; Richard, P.; Poli, R.; Jenny, T.; Savary, C. *Inorg. Chim. Acta* **2006**, *359*, 4447. (e) Stoffelbach, F.; Poli, R.; Maria, S.; Richard, P. *J. Organomet. Chem.* **2007**, *692*, 3133.

(31) (a) Laine, T. V.; Klinga, M.; Maaninen, A.; Aitola, E.; Leskela, M. *Acta Chem. Scand.* **1999**, *53*, 968. (b) Cope-Eatough, E. K.; Mair, F. S.; Pritchard, R. G.;

Warren, J. E.; Woods, R. J. *Polyhedron* **2003**, *22*, 1447. (c) El-Ayaan, U.; Paulovicova, A.; Fukuda, Y. *J. Mol. Struct.* **2003**, *645*, 205.

(32) Labauze, G.; Samuel, E.; Livage, J. *Inorg. Chem.* **1980**, *19*, 1384.

(33) We conducted the reaction of styrene with Ph_2CCl_2 catalyzed by **1a** (3 mol%) in C_6D_6 at 100 ºC for 14 h, and the corresponding product was generated in 58% yield.

(34) Laguerre, M.; Dunogues, J.; Calas, R.; Duffaut, N. *J. Organomet. Chem.* **1976**, *112*, 49.

(35) (a) Dieck, H.; Svoboda, M.; Greiser, T. Z. *Naturforsch. B* **1981**, *36*, 823.

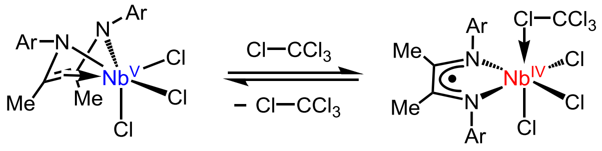
(36) Bruker, *SAINT-Plus*, Bruker AXS Inc., Madison, Wisconsin, USA, **1999**.

(37) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(38) Sheldrich, G. M. *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, **2008**, *64*, 112.

(39) Farrugia, L. J. J. *Appl. Crystallogr.* **1999**, *32*, 837.

TOC Graphic



η^4-(σ^2,π) coordination mode

κ^2-(*N*,*N'*) coordination mode

active species for

radical addition reaction