Remote and α-Thio Carbene Complexes Derived from an Oxazolinyl-substituted Thiophene

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Dedicated to Professor Wolfgang Beck on the occasion of his 80th birthday in recognition of his many contributions to inorganic and organometallic chemistry

Transmetallation and oxidative substitution were utilized to prepare examples of group 14, group 6 and group 10 complexes from lithiated or chlorinated 4,4-dimethyl-2-(2-thienyl) oxazoline or its *N*-alkylated analogs. Two of the product types (**2** and **5**) can be classified as α-thio or *remote* carbene complexes, depending on the position (3- or 5-) of attachment to the substituted thiophene ring. Spectroscopic measurements as well as crystal and molecular structure determinations clarified the bonding within the new compounds.

Key words: Carbene Complexes, Thienylidene Complexes, *remote* Carbenes, Chromium, Palladium

Introduction

The selective deprotonation of 4,4-dimethyl-2-(2-thienyl) oxazoline (**I**, Fig. 1) to afford 3- or 5- lithiated compounds was studied in the 1970s by Vecchia and Vlattas [1], and later by Carpenter, Chadwick and Ennis [2]. In the early 1990s, Das and co-workers used *trans*-metallation to prepare, and then crystallographically authenticate a number of tin(IV) compounds in which the same anionic ligand is bonded in both bidentate [3] and monodentate [4] fashion (compare **II** and **III**, Fig. 1).

Subsequently, transition metal complexes, also originating from the substituted thiophene above, have been reported [5, 6] and the crystal structure of **IV** determined [6]. Notably, the dinuclear complex can be represented as a coordinated carbene by one of its valence bond contributing structures. ^{13}C NMR studies of all these complexes strongly indicate the presence of a coordinating carbene carbon atom. Carbene complexes in which the conjugated heteroatom is positioned remotely from the carbene carbon atom have lately attracted the attention of preparative and theoretical chemists, and have found application in homogeneous catalysis [7]. The fact that metal complexes derived from **I** exhibit carbene character prompted us to embark on the preparation of mononuclear carbene-like complexes from the same source, in which the heteroatoms occur α to or distant from the carbene carbon atoms. In this paper, we i) report the preparation of such complexes using metal exchange and oxidative methods; ii) describe the crystal and molecular structures of the new compounds; iii) characterize and discuss the bonding in the new compounds in terms of their most important mesomeric structures.

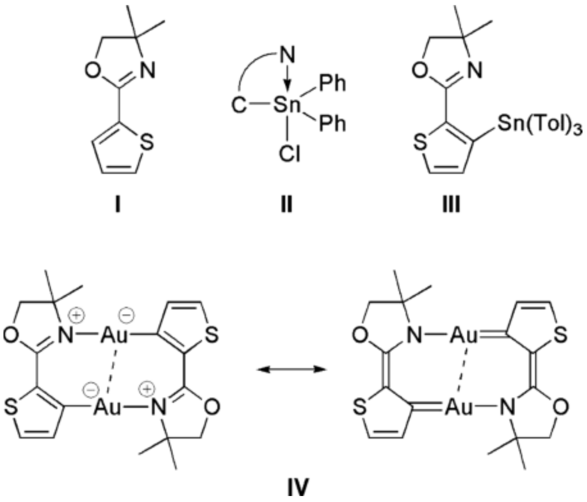
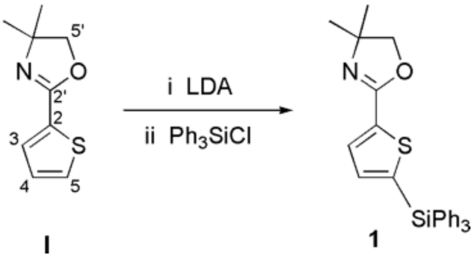


Fig. 1. Complexes previously prepared from **I** and characterized by single-crystal X-ray diffraction; $\widehat{\mathrm{CN}} = \overbrace{\mathrm{CCH{=}CHSC}}\underbrace{\mathrm{COCH_2C(CH_3)_2N}}$.



Scheme 1.

Results and Discussion

Synthetic procedures

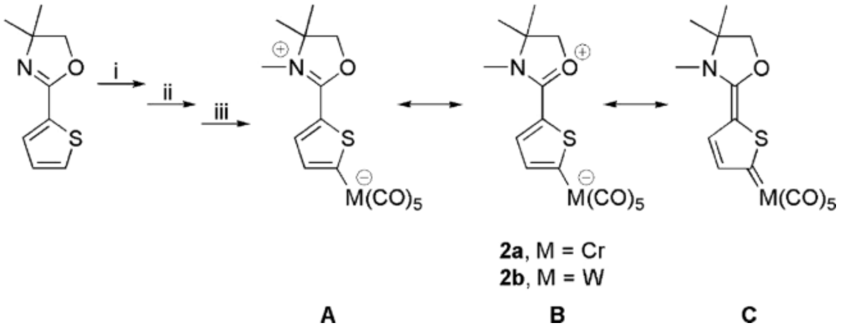
A main group derivative of **I**, compound **1**, was prepared by selective deprotonation in position 5 followed by the exchange of Li^+ for Ph_3Si^+ (Scheme 1).

Attempted deprotonation of **1** followed by treatment with $[Cr(CO)_5Br]NEt_4$ failed to afford an isolable product, and **1** is hence only used as a reference in structural comparisons. Treatment of **I** with *n*-BuLi and then with $[M(CO)_5X]NEt_4$ (M = Cr or W; X = Br or Cl) in THF yielded dark-yellow solutions. The crude mixtures were stripped of solvent and alkylated in CH_2Cl_2 with $CF_3SO_3CH_3$. The desired neutral products, orange **2a** and **2b** (Scheme 2), were obtained in crystalline form (**2a** suitable for crystal structure determination) after silica gel separation and recrystallization from CH_2Cl_2/pentane. The two complexes are soluble in more polar organic solvents such as THF and CH_2Cl_2, but less so in ether and hexane.

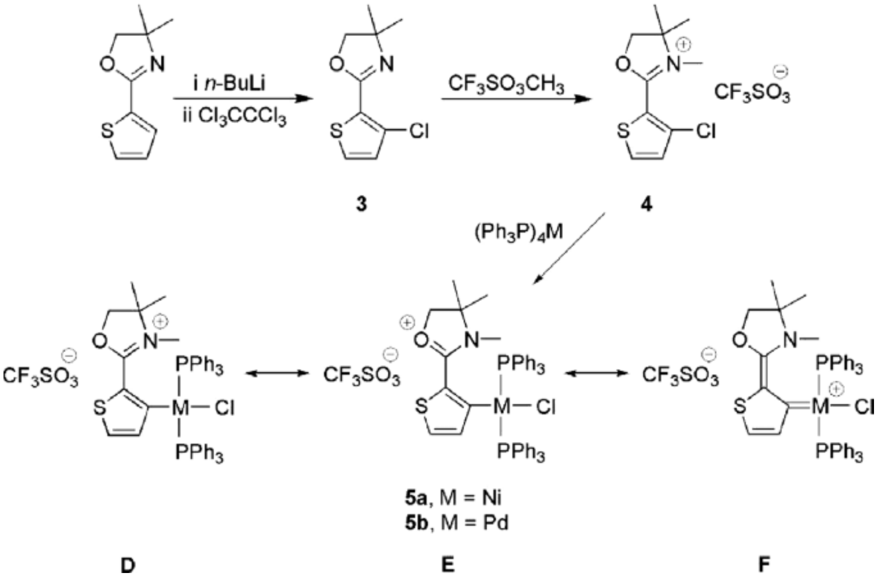
Consecutive deprotonation, chlorination and alkylation of precursor **I**, achieved by using *n*-BuLi, Cl_3CCCl_3 and $CF_3SO_3CH_3$, afforded first compound **3** and then compound **4** (Scheme 3). The other targeted complexes **5a** and **5b** (Scheme 3) were formed in high yields during an oxidative substitution reaction of **4** with $(Ph_3P)_4M$ (M = Ni or Pd). These cationic complexes are insoluble in diethyl ether and alkanes but soluble in methylene chloride. Colorless crystals of **5b**, suitable for a single-crystal X-ray analysis, were obtained by slow vapor diffusion of pentane into a concentrated CH_2Cl_2 solution of the complex.

Spectrometric and spectroscopic characterization

The EI mass spectra of **2a** and **2b** clearly show the successive loss of five CO groups from the molecular ion. The infrared spectra of these two complexes in the carbonyl region are very similar (ν_{CO}: 2045 ($A_1^{(1)}$), 1918 (E), 1881 ($A_1^{(2)}$) and 2052 ($A_1^{(1)}$), 1914 (E), 1881 ($A_1^{(2)}$) cm^{-1}, respectively) and their



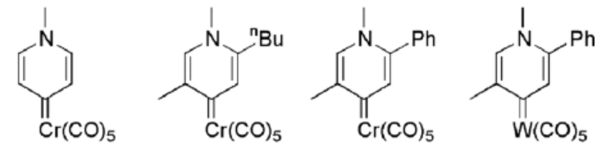
Scheme 2. i) *n*-BuLi; ii) $[(CO)_5MX]NEt_4$/THF (M = Cr, X = Br; M = W, X = Cl); iii) $CF_3SO_3CH_3/Cl_2Cl_2$.



Scheme 3.

similarity to the CO frequencies observed for the known *remote* and *normal* pyridylidene complexes **V–VIII** in Fig. 2 (average ν_{CO} for chromium complexes: 2042 ($A_1^{(1)}$), 1915 (E); ν_{CO} for the tungsten complex: 2052 ($A_1^{(1)}$), 1914 (E) cm^{-1}) [8] cannot be overlooked. This correspondence with diorganocarbene complexes is also obvious in the carbonyl ^{13}C NMR resonances that occur at δ = 226 (*trans*) and δ = 221 (*cis*) for the chromium, and at δ = 206 (*trans*) and δ = 201 (*cis*) for the tungsten complexes. The chemical shifts for the coordinated carbons in **2a** and **2b** (δ = 218 and δ = 200) are somewhat lower than in the pyridylidene complexes (Fig. 2), but still indicate significantly increased carbon deshielding compared to C^5 (δ = 138) in the nonalkylated silicon analog **1** (Scheme 1). The contributing structure **C** (Scheme 2) deserves a role in the description of these products.

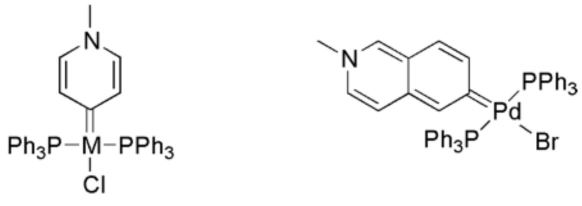
The positive-ion FAB mass spectra of the group 10 complexes **5a** and **5b** display signals that indicate the presence of the cationic complexes as well as fragments owing to the sequential loss of a PPh_3 ligand and a Cl atom. Two-dimensional NMR techniques (ghsqc and ghmqc) were employed to assign the resonances observed in the ^{1}H and ^{13}C NMR spectra of compounds **3**, **4** and **5**. The ^{13}C NMR spectra of **5a** and **5b** compared to the cationic precursor **4** indicate significant deshielding of the C^3 carbons in the modified thiophene ring upon complexation with $\Delta\delta$ values of *ca.* 50 ppm. Their coordinated carbon resonances of δ = 187 and δ = 183, respectively, compare well with those in *remote* one-*N* heterocyclic carbene complexes (such as **XI** [9, 7c] and **XII** [10], Fig. 3) that typically occur between δ = 180 and δ = 210. The resonance structures **D–F** (combined) describe the bonding in **5a** and **5b**.



V **VI** **VII** **VIII**

ν_{CO}/cm :	2044, 1917	2040, 1911	2041, 1916	2052, 1914
$\delta(C_{carb})$:	241	232	238	219
$\delta(C_{CO})$:	226 (*trans*), 220 (*cis*)	226, 221	226, 220	206, 202

Fig. 2. Characterization data for pyridylidene complexes of group 6 metals.



XIa, M = Ni : $\delta(C_{carb})$ 205 **XII** : $\delta(C_{carb})$ 187

XIb, M = Pd : $\delta(C_{carb})$ 198

Fig. 3. ^{13}C NMR chemical shifts (in ppm) for three remote diorganocarbene complexes of selected group 10 metals.

The metal-carbon double bonds drawn in the schemes should not be taken too literally – they only serve to indicate the involvement of carbene complex formation. No direct measure of the amount of metal-C π bonding is available. The final indication of the best applicable mesomeric structures for the new compounds emerged from crystal and molecular structure determinations, and is discussed below.

Crystal and molecular structures

Only a few structural reports of oxazolinyl thiophenes or their derivatives are available. To the best of our knowledge, only three encompass purely organic compounds [11] and five involve metal atoms. Two of the latter represent more classical coordination compounds with an imine N atom from the oxazoline ring bonded to a metal ion [12]. The remaining three (**II**–**IV**), mentioned earlier in the text, embrace triorganotin(IV) [3], tetraorganotin(IV) [4] and a gold(I) complex with carbene character [6].

The new compound **1** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Fig. 4 [13]). The bond lengths in the organosilyl unit as well as those in the heterocyclic moiety correspond well with reported data [11, 14] and are reflected in the representation in Scheme 1. Whereas the thiophene ring is planar (rms deviation = 0.0046 Å) as expected, the oxazoline ring deviates somewhat from planarity (0.065(2) Å) like the corresponding ring in [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]tris(p-tolyl)tin (0.055(7) Å). The torsion angles C4–C3–C6–N7 and C4–C3–C6–O10 have values of 172.9(4)° and $-7.5(5)$°, respectively.

The molecules interact through weak C–H···N and C–H···π hydrogen bonds. These interactions, namely C9–H9B···N7 (C···N = 3.481(5) Å (symmetry operator: $1-x$, $-1/2+y$, $1/2-z$) and C17–H17···Cg1 (Cg1 is the centroid of the C20–C25 phenyl ring, C···Cg = 3.723(4) Å, symmetry operator: x, $1+y$, z) involve the oxazoline rings from adjacent molecules and phenyl rings from neighboring triphenylsilyl units, respectively, and result in the formation of 1D strands expanding along the crystallographic b axis. (Supporting Information, Fig. S1). Despite the presence of many aromatic rings no $\pi-\pi$ interactions are present and the packing is further stabilized by van der Waals interactions.

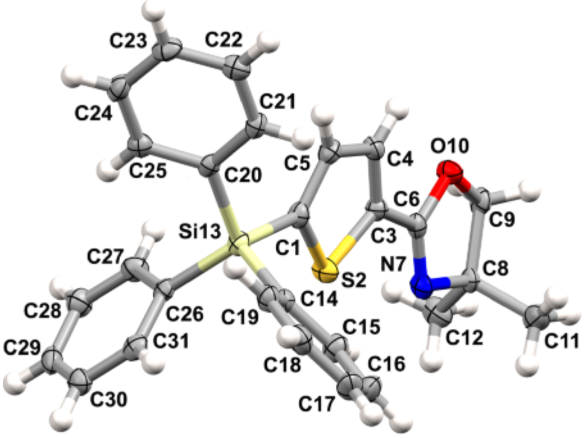


Fig. 4 (color online). Molecular structure of compound **1** with displacement ellipsoids drawn at the 50 % probability level.

Compound **2a** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. Five carbonyl ligands, and the carbene carbon atom orginating from the thiophene ring form a distorted octahedral geometry around the central Cr atom. The bond lengths of the two kinds of Cr–C bonds that determine the coordination geometry around the metal atom are in good agreement with earlier reports [15]. Bond lengths and angles are presented in the caption of Fig. 5.

The bond lengths in the heterocyclic ligand of complex **2a** differ from those in compound **1** (Table 1) indicating internal rearrangement of the π electron distribution as a result of alkylation and complex formation. Shorter C3–C6 and C4–C5 bonds, as well as an elongation of the C1–C5, C3–C4 and C6–N7 distances clearly indicate double bond character between the two heterocyclic rings (represented by the mesomeric form **C** in Scheme 2). Applying the program

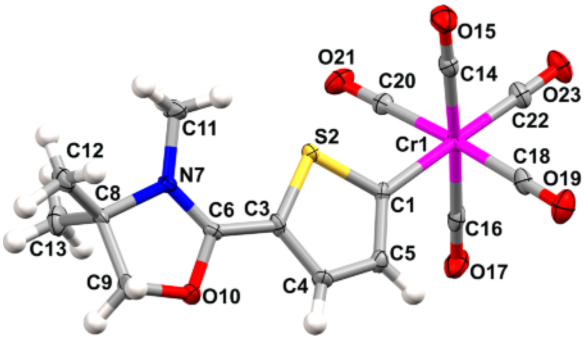


Fig. 5 (color online). Molecular structure of **2a**, with displacement ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Cr1–C22 1.864(3), Cr1–C16 1.898(3), Cr1–C20 1.898(3), Cr1–C14 1.899(3), Cr1–C18 1.910(3), Cr1–C1 2.108(3); C22–Cr1–C16 91.88(13), C22–Cr1–C20 91.41(13), C16–Cr1–C20 88.96(13), C22–Cr1–C14 91.08(13), C16–Cr1–C14 176.83(13), C20–Cr1–C14 89.86(13), C22–Cr1–C18 92.46(13), C16–Cr1–C18 90.43(13), C20–Cr1–C18 176.10(13), C14–Cr1–C18 90.55(13), C22–Cr1–C1 178.94(12), C16–Cr1–C1 87.23(12), C20–Cr1–C1 89.16(12), C14–Cr1–C1 89.81(12), C18–Cr1–C1 86.96(11).

Table 1. Selected bond lengths (Å) for the heterocyclic ligands in **1**, **2a** and **5b** with estimated standard deviations in parentheses.

	1	**2a**	**5b**
Connectivity			
C3–C6	1.458(4)	1.417(4)	1.436(7)
C6–N7	1.271(4)	1.313(3)	1.284(6)
C6–O10	1.363(4)	1.341(3)	1.317(6)
C3–C4	1.354(4)	1.388(4)	1.379(6)
C4–C5	1.418(4)	1.391(4)	1.410(6)
C1–C5	1.376(4)	1.399(4)	1.346(8)

MOGUL 1.4 [16] starting from contributing structure **C**, shows that many of the relevant bond lengths of the heterocyclic ligand are found at the extremes of the distribution chart. More specifically, C3–C6 and C4–C5 appear in the longest double bond range, whereas C1–C5 and C6–O10 are located at the shortest single bond end. These results, combined with a C6–N7 bond length of 1.313(3) Å – a value way too short for being a 'pure' single bond – and a shorter C6–O10 bond (1.341(3) Å) than in **1** (1.363(4) Å), suggest significant contributions of additional mesomeric forms **A** and **B** (Scheme 2) with zwitterionic structure **A** predominant. With the thiophene ring once more planar (rms = 0.0007 Å), the oxazoline ring shows a much higher deviation from planarity than in **1**, and the atom C9 deviates 0.165(2) Å from the ring's mean plane. The torsion angles C4–C3–C6–N7 and C4–C3–C6–O10 measure 176.5(3)° and −5.9(5)°, respectively. The packing of the molecules is controlled by an abundance of weak C–H···π and C–H···O hydrogen bonds that involve all methyl groups as well as the thiophene ring and carbonyl groups, affording a 3D supramolecular assembly.

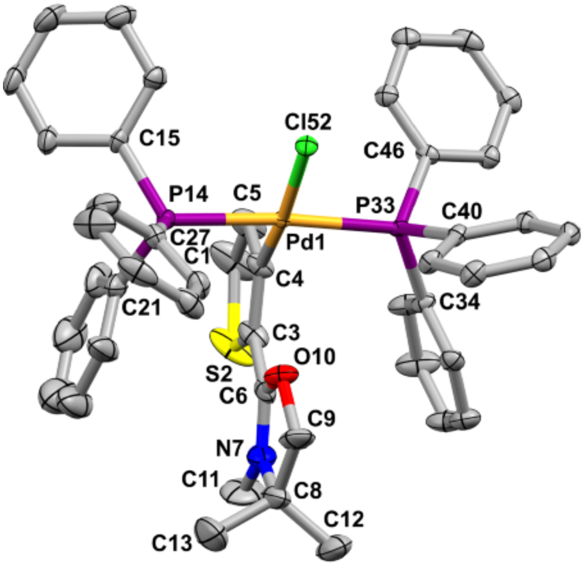


Fig. 6 (color online). Representation of the cationic Pd(II) complex in **5b** with displacement ellipsoids drawn at the 50% probability level; hydrogen atoms in the complex and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1–C4 1.992 (4), Pd1–P14 2.326(1), Pd1–P33 2.329(1), Pd1–Cl52 2.366(1); C4–Pd1–P14 89.29(13), C4–Pd1–P33 88.41(13), P14–Pd1–P33 175.27(4), C4–Pd1–Cl52 170.27(13), P14–Pd1–Cl52 90.64(4), P33–Pd1–Cl52 92.33(4).

Compound **5b** crystallizes as a dichloromethane solvate in the orthorombic space group $P2_12_12_1$ with one cationic Pd(II) complex, one triflate counterion and two dichloromethane molecules in the asymmetric unit. The slightly distorted square-planar geometry around the metal atom is formed by the two P atoms of the triphenylphosphine ligands that have adopted a *trans*-configuration, the carbene carbon atom from the thiophene ring and one chloride ion. Selected bond lengths and angles for compound **5b** are presented in the caption of Fig. 6.

The coordination sphere around the metal center conform with reported values for similar square-planar complexes [7c, 17]. A Cambridge Database query and comparison with bond lengths for simi-

Table 2. Crystal structure data for **1**, **2a** and **5b**.

	1	**2a**	**5b** $\cdot$ 2CH$_2$Cl$_2$
Formula	$C_{27}H_{25}NOSSi$	$C_{15}H_{13}CrNO_6S$	$C_{46}H_{43}ClNOP_2PdS$ $\cdot CF_3O_3S\cdot 2(CH_2Cl_2)$
M_r	439.63	387.32	1180.59
Crystal shape	block	block	needle
Crystal size, mm^3	$0.12 \times 0.10 \times 0.10$	$0.15 \times 0.10 \times 0.10$	$0.27 \times 0.07 \times 0.05$
Temperature, K	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
a, Å	9.831(2)	9.4279(17)	15.0432(9)
b, Å	9.0705(18)	14.331(3)	18.1747(11)
c, Å	27.335(6)	12.646(2)	18.4051(12)
β, deg	107.62(3)	94.798(3)	90.00
V, Å^3	2323.2(8)	1702.7(5)	5032.1(5)
Z	4	4	4
$D_{\text{calcd.}}$, g cm^{-3}	1.26	1.51	1.56
μ (MoK_α), cm^{-1}	2.1	8.2	8.4
$F(000)$, e	928	792	2400
hkl range	$-10 \le h \le 11$	$-12 \le h \le 12$	$-12 \le h \le 18$
	$-11 \le k \le 8$	$0 \le k \le 18$	$-22 \le k \le 22$
	$-33 \le l \le 31$	$0 \le l \le 16$	$-22 \le l \le 22$
$((\sin\theta)/\lambda)_{\max}$, Å^{-1}	0.6073	0.6666	0.6265
Refl. measd/unique/R_{int}	11841/4290/0.065	6190/6190/0.0	28597/10236/0.028
Param. refined	282	221	608
$R(F)/wR(F^2)^{\text{a}}$ ($I > 2\sigma(I)$)	0.0547/0.1025	0.0574/0.1382	0.0428/0.1099
$R(F)/wR(F^2)^{\text{a}}$ (all refl.)	0.1013/0.1275	0.0689/0.1438	0.0449/0.1118
GoF $(F^2)^{\text{b}}$	1.066	1.079	1.036
$\Delta\rho_{\text{fin}}$ (max/min), e Å^{-3}	0.454/ − 0.559	0.917/ − 0.454	1.315/ − 0.684

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (\mathrm{A}P)^2 + \mathrm{B}P]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

lar structures (MOGUL), clearly indicate the iminium form **D** (Scheme 3) as the dominant mesomeric representation for this compound. It is worth mentioning that the rather short C6–O10 distance (1.317(6) Å) – compared also to the same separation in **1** and **2a** – points at an increased contribution of the oxonium Lewis structure **E** owing to alkylation and cationic complex formation. The thiophene ring remains planar (rms deviation = 0.0064 Å), and the oxazoline ring shows a somewhat smaller deviation from planarity than in **1** and **2b** (the biggest deviation from the ring's mean plane is −0.060(3) Å for C9). The C4–C3–C6–N7 and C4–C3–C6–O10 torsion angles with values of −178.2(5)° and 2.9(7)° indicate an essentially planar arrangement of the two heterocyclic rings.

The complex cations are associated through a network of weak C–H···π and C–H···Cl interionic interactions. These interactions, namely C30–H30···Cg1 (Cg1 is the centroid of the phenyl ring C46–C51, C···Cg1 = 3.589(6) Å, symmetry operator: $3/2 - x$, $1 - y$, $-1/2 + z$), C38–H38···Cg1 (C···Cg1 = 3.576(6) Å, symmetry operator: $1/2 + x$, $1/2 - y$, $1 - z$), and C1–H1···Cl52 (C···Cl = 3.451(2) Å, symmetry operator: $3/2 - x$, $1 - y$, $1/2 + z$) involve three of the phenyl groups, the thiophene ring and the coordinated Cl, resulting in the formation of a 3D supramolecular assembly. The solvent molecules and counterions (for labelling see Supporting Information, Fig. S2) located within the voids of this supramolecular aggregation, further interact through association C64–H64B···Cg4 (Cg4 is the centroid of the phenyl ring C34–C39, C···Cg4 is 3.656(8) Å, symmetry operator: $-1/2 + x$, $1/2 - y$, $1 - z$), C64–H64A···Cl52 (C···Cl = 3.498(6) Å), C19–H19···O54 (C···O = 3.452(7) Å, symmetry operator: $1 - x$, $1/2 + y$, $3/2 - z$) and C48–H48···O55 (C···O = 3.455(5) Å, symmetry operator: $1 - x$, $-1/2 + y$, $3/2 - z$). The sections of the cationic complex involved in weak interactions form channels down the C axis, with the free space then occupied by oxazolidine rings, solvent molecules and counterions (a packing diagram is shown in the Supporting Information, Fig. S3).

Conclusions

Stable transition metal complexes that can be formulated on the basis of physical and crystallographic evidence as the first examples of either α-thio or *remote* thiophenylidene(thienylidene) complexes – depending on the position (5 or 3) of attachment to the thiophene ring in an alkylated 4,4-dimethyl-2-(2-thienyl)oxazoline system – can be readily prepared. However, N and O involvement in π bonding within the oxazolidine ring, and represented by iminium or oxonium zwitterionic or ionic structural complex variants, is an outstanding feature of the new complexes. The double bond to N dominates, and the relative contribution of the oxonium mesomeric structure is dependent upon the positioning of the chosen metal fragment and the charge on the resulting complex. Future investigations should be directed towards the preparation of *remote*, *abnormal* carbene complex analogs (with the metal coordination occurring in position 4 of the thiophene ring) and a comparison of the bonding in such complexes with that of the existing ones.

Experimental Section

All reactions were carried out under nitrogen or argon using standard vacuum line and Schlenk techniques. All solvents were freshly distilled under an inert atmosphere before use. THF, diethyl ether, pentane, and hexane were dried over KOH and distilled over sodium wire. Benzophenone was used as an indicator in THF and diethyl ether, and benzophenone in conjunction with triglyme in pentane and hexane. Dichloromethane was dried over KOH and distilled over CaH_2 [18]. The starting materials, 2-(4,4-dimethyl-1,3-oxazolin-2-yl)thiophene [2a], $[Cr(CO)_5Br][NEt_4]$ [19a], $[W(CO)_5Cl][NEt_4]$ [19b] and $Pd(PPh_3)_4$ [20] were prepared according to literature procedures. All the other starting materials are commercially available and were used without further purification.

Melting points were determined on a Stuart SMP3 apparatus and are uncorrected. Mass spectra were recorded on a AMD 604 (EI, 70 eV) or VG 70 SEQ (FAB, 70 eV, *m*-nitrobenzyl alcohol matrix) instrument, and NMR spectra on a Varian 300 FT or INOVA 600 MHz spectrometer (^1H NMR at 300/600 MHz, $^{13}C\{^1H\}$ NMR at 75/150 MHz and $^{31}P\{^1H\}$ NMR at 121.5/243 MHz; δ reported relative to the solvent resonance or external reference, 85 % H_3PO_4). Elemental analyses were carried out at the Department of Chemistry, University of Cape Town, South Africa. The products were subjected to high vacuum for 5 h before analysis.

*2-[5-(Triphenylsilyl)thiene-2-yl]-4,4-dimethyl-1,3-oxazoline (**1**)*

The synthesis of this complex was based on literature procedures [2a]. A solution of LDA (3.3 mL, 1.4 M, 4. 8 mmol *n*-BuLi and 0.48 g, 0.67 mL, 4.8 mmol diisopropylamine) in hexane was added slowly to a solution of 2-(4,4-dimethyl-1,3-oxazolin-2-yl)thiophene, **I** (0.83 g, 4.6 mmol) in THF at −78 °C. This mixture was stirred for 30 min at −78 °C, Ph_3SiCl (1.4 g, 4.7 mmol) was added and the mixture was stirred for an additional 30 min at −78 °C, where after it was allowed to slowly warm up to room temperature. The solvent was removed *in vacuo*. The product was adsorbed onto silica gel and eluted at room temperature with CH_2Cl_2/hexane (2 : 1) to obtain 0.78 g (39 %) of the colorless compound **1**. Crystals suitable for a single-crystal X-ray structure determination to confirm the position of the $SiPh_3$ group were obtained by slow evaporation of a concentrated CH_2Cl_2 solution. M. p. 128–129 °C. – ^1H NMR (CD_2Cl_2): δ = 7.59, 7.48, 7.41 (3 × m, 15H, Ph), 7.64 (d, 1H, ^3J = 3.8 Hz, H^3), 7.30 (d, 1H, ^3J = 3.8 Hz, H^4), 4.08 (s, 2H, $H^{5'}$), 1.32 (s, 6H, Me). – ^{13}C NMR (CD_2Cl_2): δ = 157.6 (s, $C^{2'}$), 139.8 (s, C^2), 138.7 (s, C^4), 138.0 (s, C^5), 136.3 (s, *ortho*-Ph), 130.4 (s, *para*-Ph), 131.1 (s, C^3), 128.3 (s, *meta*-Ph), 128.2 (s, *ipso*-Ph), 79.7 (s, $C^{5'}$), 68.3 (s, $C^{4'}$), 28.3 (s, Me). – MS (FAB, 70 eV): *m*/*z* (%) = 440.3 (100) $[M]^+$, 424.2 (12) $[M–Me]^+$, 362.2 (20) $[M–Ph]^+$, 259.2 (25) $[Ph_3Si]^+$. – $C_{27}H_{25}NOSSi$ (439.14): (%) calcd. C 73.76, H 5.73, N 3.19; found C 73.57, H 5.68, N 3.24.

*Pentacarbonyl[(3,4,4-trimethyl-1,3-oxazolidin-2-ylidene)-2(5H)-thien-5-ylidene]chromium(0) (**2a**)*

A solution of **I** (0.22 g, 1.2 mmol) in THF was treated with *n*-BuLi in hexane (0.9 mL, 1.3 mmol, 1.5 M) at −78 °C for 15 min. The temperature was raised to −30 °C, and the yellow reaction mixture was stirred for 40 min. After the addition of $[(CO)_5CrBr][NEt_4]$ (0.49 g, 1.2 mmol) dissolved in THF (at −30 °C) the reaction mixture was stirred for 2 h followed by the solvent removal under vacuum. The residue was dissolved in CH_2Cl_2, cooled down to −50 °C, and $CF_3SO_3CH_3$ (0.14 mL, 1.2 mmol) was added drop by drop. The reaction mixture was allowed to reach room temperature slowly, then filtered over dried silica (2 cm) and dried under vacuum. The residue was chromatographed on a flash silica column at −15 °C with hexane/ether (1:1) as eluent, and the product **2a** 0.020 g, (6.0 %) was removed from the column with CH_2Cl_2 after all the other fractions were washed out. Crystallization from a CH_2Cl_2/pentane solution (−20 °C) gave yellow crystals of complex **2a** suitable for single-crystal X-ray structure determination. Yield: 0.02 g, 6.0 %. M. p. 154–160 (dec.) °C. – IR (CH_2Cl_2): $\nu(CO)$ = 2045 (m, $A_1^{(1)}$), 1918 (s, E), 1881 (sh, $A_1^{(2)}$) cm^{-1}. – ^1H NMR (CD_2Cl_2):

δ = 7.93 (d, 1H, ^3J = 3.7 Hz, H^3), 7.54 (d, 1H, ^3J = 3.7 Hz, H^4), 4.52 (s, 2H, H$^{5'}$), 3.41 (s, 3H, NMe), 1.48 (s, 6H, Me). – ^{13}C NMR (CD_2Cl_2): δ = 226.2 (s, CO$_{\text{trans}}$), 220.6 (s, CO$_{\text{cis}}$), not observed (s, C^5), not observed (s, C$^{2'}$), 143.2 (s, C^2), 138.5 (s, C^3), 132.9 (s, C^4), 80.1 (s, C$^{5'}$), 66.5 (s, C$^{4'}$), 29.6 (s, NMe), 24.1 (s, Me). – MS (FAB/EI, 70 eV): m/z (%) = 387 (9) [M]$^+$, 359 (3) [M–CO]$^+$, 331 (5) [M–2CO]$^+$, 303 (4) [M–3CO]$^+$, 275 (9) [M–4CO]$^+$, 247 (6) [M–5CO]$^+$, 196 (36) [2-(4,4-dimethyl-1,3-oxazolin-2-yl)thiophene]$^+$. – $C_{15}H_{13}NO_6SCr$ (378.33): (%) calcd. C 46.51, H 3.38, N 3.62; found C 46.33, H 3.29, N 3.58.

*Pentacarbonyl[(3,4,4-trimethyl-1,3-oxazolidin-2-ylidene)-2(5H)-thien-5-ylidene]tungsten(0) (**2b**)*

A solution of **I** (0.56 g, 3.1 mmol) in THF was treated with *n*-BuLi in hexane (2.3 mL, 3.7 mmol, 1.6 M) at −78 °C for 15 min. The temperature was raised to −30 °C, and the yellow reaction mixture was stirred for 30 min. After the addition of [(CO)$_5$WCl][NEt$_4$] (1.6 g, 3.1 mmol) dissolved in THF (at −30 °C) the reaction mixture was stirred for 2 h. The temperature was lowered to −50 °C, and $CF_3SO_3CH_3$ (0.35 mL, 3.1 mmol) was added drop by drop. The reaction mixture was stirred for 30 min at −50 °C, allowed to reach room temperature slowly, and the solvent removed under vacuum. The dark-yellow residue was dissolved in CH_2Cl_2, filtered through a short florisil column and dried under vacuum. Column chromatography on flash grade silica gel with CH_2Cl_2-hexane (5:2) at −15 °C yielded an orange product. This fraction was not pure and was dissolved in diethyl ether, filtered through dried flash grade silica gel and washed with ether to further remove impurities. The product was eluted from the column with CH_2Cl_2. Crystallization from a CH_2Cl_2/pentane solution (−20 °C) gave yellow crystals of complex **2b** suitable for single-crystal X-ray structure determination. Yield: 0.16 g, 10 %. M. p. 175 (dec.) °C. – IR (CH_2Cl_2): ν(CO) = 2054 (m, $A_1^{(1)}$), 1958 (w, B_1), 1914 (s, E), 1881 (sh, $A_1^{(2)}$) cm^{-1}. – ^{1}H NMR (CD_2Cl_2): δ =7.86 (d, 1H, ^3J = 3.7 Hz, H^3), 7.60 (d, 1H, ^3J = 3.7 Hz, H^4), 4.53 (s, 2H, H$^{5'}$), 3.41 (s, 3H, NMe), 1.49 (s, 6H, Me). – ^{13}C NMR (CD_2Cl_2): δ = 205.8 (s, $J_{\text{W–C}}$ = 136.2 Hz, CO$_{\text{trans}}$), 200.5 (s, $J_{\text{W–C}}$ = 125.9 Hz, CO$_{\text{cis}}$), 200.3 (s, C^5), 161.0 (s, C$^{2'}$), 143.9 (s, C^2), 139.4 (s, C^3), 122.1 (s, C^4), 80.2 (s, C$^{5'}$), 66.6 (s, C$^{4'}$), 29.7 (s, NMe), 24.1 (s, Me). – MS (FAB/EI, 70 eV): m/z (%) = 519 (9) [M]$^+$, 491 (4) [M–CO]$^+$, 463 (5) [M–2CO]$^+$, 435 (7) [M–3CO]$^+$, 196 (36) [2-(4,4-dimethyl-1,3-oxazolin-2-yl)thiophene]$^+$. – $C_{15}H_{13}NO_6SW$ (519.17): (%) calcd. C 34.70, H 2.52, N 2.70; found C 34.17, H 2.48, N 2.75.

*2-[3-Chlorothiene-2-yl]-4,4-dimethyl-1,3-oxazoline (**3**)*

A 2.0 mL solution of *n*-BuLi in hexane (3.0 mmol, 1.5 M) was diluted by 10 mL diethyl ether, cooled to −50 °C, and 0.487 g (2.69 mmol) **I** in 10 mL of diethyl ether was added slowly over a period of 1 min. The cooling bath was replaced by another one (−10 °C), and the solution was stirred for 10 min. The mixture was then cooled to −80 °C, and 0.64 g (2.7 mmol) of hexachloroethane [21] dissolved in 15 mL diethyl ether was added over a period of 25 min, ensuring that the temperature never rose above −60 °C. After addition, the temperature was allowed to warm up to −20 °C, and 50 mL of water was added while the solution was stirred vigorously. The mixture was extracted with diethyl ether (3 × 20 mL), the organic layer dried over $MgSO_4$ and filtered. The product mixture was column chromatographically (silica gel) separated at room temperature with CH_2Cl_2 as eluent to give 0.28 g (47 %) of colorless **3** and 0.060 g of unreacted **1**. M. p. 49–51 °C. – ^{1}H NMR (CD_2Cl_2): δ = 7.40 (d, 1H, ^3J = 5.3 Hz, H^5), 6.98 (d, 1H, ^3J = 5.3 Hz, H^4), 4.08 (s, 2H, H$^{5'}$), 1.34 (s, 6H, Me). – ^{13}C NMR (CD_2Cl_2): δ = 156.3 (s, C$^{2'}$), 130.0 (s, C^4), 128.4 (s, C^5), 127.3 (s, C^3), 124.3 (s, C^2), 79.5 (s, C$^{5'}$), 68.3 (s, C$^{4'}$), 28.3 (s, Me). – MS (FAB, 70 eV): m/z(%) = 218.1 (36) [M+H (^{37}Cl)]$^+$, 216.1 (100) [M+H (^{35}Cl)]$^+$, 200.0 (13) [M–Me]$^+$. – $C_9H_{10}NOSCl$ (215.02): (%) calcd. C 50.12, H 4.67, N 6.49; found C 49.95, H 4.53, N 6.37.

*2-(3-Chlorothiene-2-yl)-3,4,4-trimethyl-1,3-oxazolinium triflate (**4**)*

Compound **4** (0.19 g, 0.51 mmol) was obtained by stirring 0.18 g (0.83 mmol) of **3** and 0.15 g (0.10 mL, 0.92 mmol) of $CF_3SO_3CH_3$ in 20 mL CH_2Cl_2 for 17 h at room temperature. The solution was concentrated until a precipitate formed, and the pinkish solvent was removed with a syringe. The resulting colorless residue was washed with diethyl ether (2 × 5 mL) and dried *in vacuo*. Yield: 0.19 g, 61 %. M. p. 125–127 °C. – ^{1}H NMR (CD_2Cl_2): δ = 8.05 (d, 1H, ^3J = 5.3 Hz, H^5), 7.23 (d, 1H, ^3J = 5.3 Hz, H^4), 4.92 (s, 2H, H$^{5'}$), 3.45 (s, 3H, NMe), 1.68 (s, 6H, Me). – ^{13}C NMR (CD_2Cl_2): δ = 166.1 (s, C$^{2'}$), 137.7 (s, C^4), 134.9 (s, C^3), 130.2 (s, C^5), 115.2 (s, C^2), 82.4 (s, C$^{5'}$), 68.9 (s, C$^{4'}$), 31.8 (s, NMe), 23.9 (s, Me). – MS (FAB, 70 eV): m/z (%) = 232.0 (43) [M–CF_3SO_3 (^{37}Cl)]$^+$, 230.0 (100) [M–CF_3SO_3 (^{35}Cl)]$^+$. – $C_{11}H_{13}NO_4S_2ClF_3$ (378.99): (%) calcd. C 34.79, H 3.45, N 3.69; found C 34.63, H 3.78, N 3.89.

*trans-Chlorobis(triphenylphosphine)[(3,4,4-trimethyl-1,3-oxazolidin-2-ylidene)-2(5H)-thien-(3H)-ylidene]nickel(II) triflate (**5a**)*

A suspension of $Ni(PPh_3)_4$ (0.26 g, 0.24 mmol) and **4** (0.085 g, 0.22 mmol) in 20 mL THF was stirred for 17 h at room temperature. The yellow precipitate in a brownish solution was filtered through celite and washed with 2 × 10 mL of toluene and 5 mL of THF. The yellow product was washed through the filter with CH_2Cl_2 to yield, after solvent evaporation, 0.17 g (79 %) of complex **5a**. Yellow plates of the complex were obtained by vapor diffusion of *n*-pentane into a CH_2Cl_2 solution of the product at −22 °C. M. p. 180.0 °C (dec.). – ^{1}H NMR (CD_2Cl_2): δ =7.55, 7.47, 7.38 (3 × m, 32H, Ph, H^4, H^5), 4.87 (s, 2H, $H^{5'}$), 2.81 (s, 3H, NMe), 1.38 (s, 6H, Me). – ^{13}C NMR (CD_2Cl_2): δ =187.4 (t, $^2J_{PC}$ = 34.2 Hz, C^3), 163.2 (s, $C^{2'}$), 136.6 (s, C^4), 135.8 (s, C^5), 134.3 (m, *ortho*-Ph), 130.4 (m, *ipso*-Ph), 130.4 (s, *para*-Ph), 128.7 (m, *meta*-Ph), 117.3 (s, C^2), 81.1 (s, $C^{5'}$), 67.9 (s, $C^{4'}$), 29.8 (s, NMe), 24.1 (s, Me). – ^{31}P NMR (CD_2Cl_2): δ = 20.82 (s, PPh_3). – MS (FAB, 70 eV): m/z (%) = 814.0 (6) [M–CF_3SO_3 (^{35}Cl, ^{58}Ni)]$^+$, 551.9 (70) [M–PPh_3–CF_3SO_3 (^{58}Ni)]$^+$, 519.3 (11) [M–PPh_3–Cl–CF_3SO_3 (^{35}Cl, ^{58}Ni)]$^+$. – $C_{47}H_{43}NO_4P_2S_2ClF_3Ni$ (961.11): (%) calcd. C 58.61, H 4.50, N 1.54; found C 59.92, H 4.71, N 1.56.

*trans-Chlorobis(triphenylphosphine)[(3,4,4-trimethyl-1,3-oxazolidin-2-ylidene)-2(5H)-thien-(3H)-ylidene]-palladium(II) triflate (**5b**)*

Compound **4** (0.038 g, 0.10 mmol) and $Pd(PPh_3)_4$ (0.12 g, 0.11 mmol) were suspended in 30 mL THF and stirred for 17 h at 60 °C. The colorless suspension in a light-yellow solution was allowed to cool to room temperature and filtered through celite. The solid on the filter was washed with THF (4 × 5 mL), dissolved in CH_2Cl_2, precipitated with hexane. After filtration solvent evaporation and recrystallization from CH_2Cl_2/hexane (−20 °C) 0.090 g (89 %) of the colorless complex **5b** was obtained. M. p. 213 °C (dec.). – ^{1}H NMR (CD_2Cl_2): δ =7.49, 7.38 (2 × m, 31H, Ph, H^4), 7.10 (d, 1H, ^3J = 4.9 Hz, H^5), 4.56 (s, 2H, $H^{5'}$), 2.92 (s, 3H, NMe), 1.36 (s, 6H, Me). – ^{13}C NMR (CD_2Cl_2): δ = 182.6 (t, $^2J_{PC}$ = 7.4 Hz, C^3), 163.8 (s, $C^{2'}$), 137.6 (s, C^4), 136.1 (s, C^5), 134.4 (m, *ortho*-Ph), 130.2 (m, *ipso*-Ph), 131.1 (s, *para*-Ph), 128.8 (m, *meta*-Ph), 116.6 (s, C^2), 80.8 (s, $C^{5'}$), 67.9 (s, $C^{4'}$), 30.2 (s, NMe), 24.1 (s, Me). – ^{31}P NMR (CD_2Cl_2,): δ = 23.20 (s, PPh_3). – MS (FAB, 70 eV): m/z (%) = 861.7 (5) [M–CF_3SO_3 (^{35}Cl, ^{106}Pd)]$^+$, 600.0 (31) [M–PPh_3–CF_3SO_3 (^{106}Pd)]$^+$, 486.0 (6) [M–PPh_3–Cl–CF_3SO_3 (^{35}Cl, ^{106}Pd)]$^+$. – $C_{47}H_{43}NO_4P_2S_2ClF_3Pd$ (1009.08): (%) calcd. C 55.85, H 4.29, N 1.39; found C 55.97, H 4.33, N 1.30.

X-Ray structure determination

Single-crystal X-ray diffraction data for **1**, **2a** and **5b** were collected on a Bruker SMART Apex [22a] diffractometer equipped with graphite monochromatized MoK_α radiation (λ = 0.71073 Å). For **1** and **5b** cell refinement and data reduction were performed using the program SAINT+ [22b]. The empirical absorption corrections were performed using SADABS [23]. The structures were solved by Direct Methods using SHELXS-97 [24] and refined by full-matrix least-squares methods based on F^2 using SHELXL-97 [24]. The crystal **2a** was found to be non-merohedrally twinned. The two components were identified using GEMINI [25], and both were simultaneously integrated using SAINT+. The data set was corrected for absorption using TWINABS [26], which was also used to create both an HKLF 4 as well as an HKLF 5 format file. The HKLF 4 format file (with the non-overlapping reflections of component 1 only) was used to solve the structure. The HKLF 5 format file was used for the refinement of the structure, BASF 0.410(1).

The program MERCURY [27] was used to prepare molecular graphic images. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions with temperature factors fixed at 1.2 times U_{eq} of the parent atoms (C, N) and 1.5 times U_{eq} for methyl groups. A summary of the data collection and structure refinement parameters is provided in Table 2. In complex **5b** anisotropic displacement parameter restraints were applied to some of the C atoms of the phenyl ring C21–C26.

CCDC 879987–879989 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information

Figures showing the weak interactions in **1** and **5b** and a packing diagram of the latter are available online (DOI: 10.5560/ZNB.2012-0118).

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