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Preparation, characterization, and reactivities of thienyl nickel complexes bearing indenyl ligands

Ruiping Wang, Laurent F. Groux, Davit Zargarian *

Département de chimie, Université de Montréal, Montréal, Quebec, Canada H3C 3J7

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Dedicated to Prof. H. Alper for his 60th birthday

Abstract

The complexes (1-R, 2-R′-indenyl)NiPPh$_3$(thienyl) (R′ = H, R = Me (**1**); Et (**2**); *i*-Pr (**3**); CH_2Ph (**4**); R′ = Ph, R = Me (**5**)) have been prepared and characterized by spectroscopic techniques and, in the case of **1**, **2** and **5**, by X-ray crystallographic studies. When combined with MAO, these compounds catalyze the polymerization of phenylacetylene to *cis*-transoidal poly(phenylacetylene) with M_w in the range of $5–7.5 \times 10^4$ Da. NMR studies have revealed that MAO methylates these complexes without ionizing the Ni–thienyl bond; this implies that the polymerization reactions likely follow a non-cationic mechanism similar to that catalyzed by the corresponding Ni–CC–Ph complexes studied previously. Complexes **1**–**5** reacted with CF_3SO_3H to produce the corresponding Ni–OSO_2CF_3 compounds by protonation at the α-C of the thienyl moiety. The compound (1-Bz–indenyl)Ni(PPh_3)(OSO_2CF_3) (**9**) has been isolated and fully characterized.

Keywords: Indenyl; Thienyl; Triflate; Polyalkynes

1. Introduction

The available data on the relative bond energies of transition metal–C bonds indicate that M–(sp-C) bonds are, in general, stronger (thermodynamically) and more stable (kinetically) than the analogous M–(sp^3-C) bonds [1]. Consistent with this trend, solid-state data have indicated that the Ni–C bond in the complexes (1-Me–Ind)(PR_3)Ni–CC–Ph [2] is shorter than the corresponding bond in the Ni–Me analogue [3]. Interestingly, however, the Ni–CC–Ph complex has a higher activity than the Ni–Me analogue in the catalytic polymerization of ethylene [4] and gives higher M_w and better yields compared with the Ni–Me and Ni–Cl analogues in the polymerization of Ph–CC–H [2]. Since mechanistic experiments have indicated that these methylaluminoxane (MAO) co-catalyzed polymerization reactions proceed by non-cationic pathways, [2,4] we reasoned that the catalytic activity of the pre-catalysts Ind(PR_3)Ni–X might be inversely proportional to the relative ease with which the X^- moiety can be abstracted by MAO. Consistent with this reasoning, NMR monitoring of mixtures of MAO and Ind(PR_3)Ni–X showed that the Ni–CC–Ph moiety was more resistant to ionization compared with the corresponding Ni–Cl and Ni–Me bonds. In addition, reaction conditions which favored the ionization of the Ni–X bond (e.g. large excess of MAO) led to lower catalytic activities and shorter polymer chains [2]. Finally, NMR experiments have indicated that the catalytically inert cations [(Ind)Ni(PPh_3)$_2$]$^+$, which form during the catalysis, tend to react more readily with $PhCC^-$ versus $^-CH_3$ to regenerate the catalytically active, neutral Ni–CR'_n complexes [5].

Taken together, these results imply that the nature of the Ni–CR'_n bond in the catalytic precursors has an important influence on the catalytic activities of these compounds. We were, thus, prompted to examine the reactivities of analogous complexes bearing Ni–(sp^2-C) bonds. Initial experiments demonstrated that the Ni–CH=CHR (R = H, Ph) and Ni–(2-pyridyl) complexes can be generated in solution but decompose during

* Corresponding author. Tel.: +1-514-343-2247; fax: +1-514-343-7586

E-mail address: zargarian.davit@umontreal.ca (D. Zargarian).

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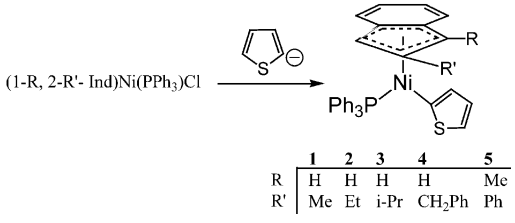
isolation, whereas the Ni–thienyl analogues were relatively easy to isolate and characterize. Therefore, we have prepared Ni–thienyl derivatives bearing differently substituted indenyl ligands and studied their reactivities. The present paper reports on the preparation of the complexes (1-R, 2-R′-indenyl)NiPPh$_3$(thienyl) (R′ = H, R = Me (**1**); Et (**2**); *i*-Pr (**3**); CH_2Ph (**4**); R′ = Ph, R = Me (**5**)) and their effectiveness in the polymerization of Ph–CC–H. The easy access to these thienyl complexes also allowed us to study the possibility of converting them to the corresponding Ni–(thienylcarbene) homologues by protonation at the β-C. These reactions led to the formation of the corresponding Ni–OSO_2CF_3 complexes instead (i.e. protonation at the α-C), as described below.

2. Results and discussion

Complexes **1**–**5** were synthesized by the metathetic reactions of the corresponding Ni–Cl precursors with a small excess of 2-thienyllithium (Scheme 1). Trituration of the oily residues obtained from the evaporation of the reaction mixture with EtOH afforded the Ni–thienyl compounds as brown powders in ca. 60–80% yields.

The spectroscopic characterization of these new complexes was quite straight forward, as follows. The ^{1}H-NMR spectra displayed most of the anticipated resonances for the three thiophenic protons (i.e. two doublets and a doublet of doublets), as well as the Ind and PPh_3 peaks characteristic of this class of compounds. For instance, the ^{1}H-NMR spectrum of **3** in acetone-d_6 displayed three distinct signals at 6.09 ppm (d, $^3J_{H-H} = 3.2$ Hz, H12), 6.63 ppm (dd, $^3J_{H-H} = 4.8$ and 3.2 Hz, H13), and 7.09 ppm (d, $^3J_{H-H} = 4.8$ Hz, H14) attributed to the thienyl moiety; these resonances are similar to those reported for the thienyl protons in Cp(NO)(PPh_3)Re(thienyl) [6] and (Tp^{Me_2})(PMe_3)Ir(thienyl)$_2$ (Tp^{Me_2} = hydridotris(2,5-dimethylpyrazolyl)borate) [7]. Moreover, the ^{1}H-NMR spectra obtained from C_6D_6 solutions of the complexes **3** and **4** displayed two different signals for the $CH(CH_3)_2$ and CH_2Ph protons, respectively, consistent with the C_1 symmetry of the complexes which renders these protons diastereotopic. The CH_2 protons in complex **2** are also diastereotopic, but they gave rise to a broad signal. On the other hand, the signals for many of the vinylic protons in the C_6D_6 spectra were poorly resolved and/or obscured by the PPh_3 resonances.

The ^{31}P{^{1}H}-NMR spectra of complexes **1**–**5** displayed singlet resonances appearing in a very narrow range of chemical shifts (ca. 37 ppm), while the ^{13}C{^{1}H}-NMR spectra confirmed the presence of the Ind and thienyl moieties. For instance, the ^{13}C{^{1}H}-NMR spectrum of complex **5** displayed the resonances due to the four thienyl carbons, two of which are doublets (C11: 141.28 ppm, $^2J_{P-C} = 28.4$ Hz; C12: 120.50 ppm, $^3J_{P-C} = 7.6$ Hz). As expected, the signals due to the quaternary carbon atoms (i.e. C11 of thienyl and C1, C3a, and C7a of Ind) are weak and broad, especially when there is a coupling to the phosphorus nucleus in the PPh_3 ligand.



Scheme 1.

2.1. Solid-state structures of *1*, *2* and *5*

The above structural assignments were confirmed by crystallographic studies on single crystals obtained for complexes **1**, **2**, and **5**; to our knowledge, these are the first crystallographically characterized thienyl complexes of nickel. Figs. 1–3 depict the solid-state structures of these complexes, while Tables 1–3 contain the crystal data and selected bond distances and angles. The overall geometry around the Ni center in these complexes is intermediate between a two-legged piano stool (assuming $\eta^3 \leftrightarrow \eta^5$-Ind) and a distorted square-planar (assuming $\eta^1,\eta^2 \leftrightarrow \eta^3$-Ind), with the largest distortion arising from the small C1–Ni–C3 angle (ca. 67°). The plane of the phenyl ring in **5** is rotated by 47.6° with respect to the five-membered ring of the Ind. The thienyl group in all three complexes is disordered over two sites related by a rotation around the Ni–C11 bond; this type of disorder has been observed in many of the previously reported structures of thienyl complexes [8]. The site

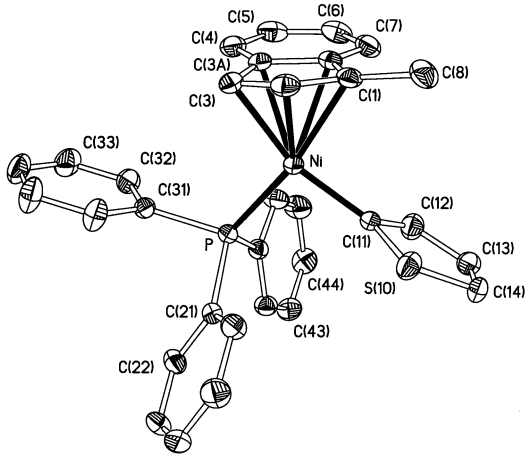


Fig. 1. ORTEP plot (30% probability ellipsoids) for the major rotamer of complex (1-Me–Ind)Ni(PPh_3)(Thienyl) (**1**). The H atoms have been omitted for clarity.

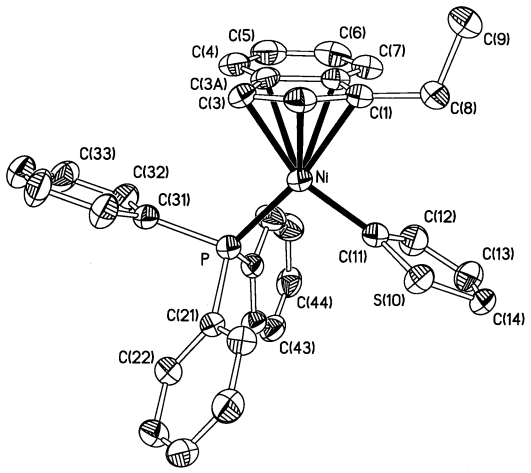


Fig. 2. ORTEP plot (30% probability ellipsoids) for the major rotamer of (1-Et–Ind)Ni(PPh_3)(Thienyl) (**2**). The H atoms have been omitted for clarity.

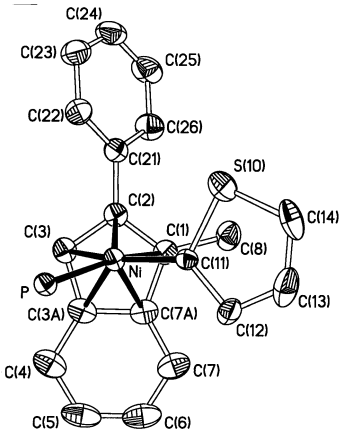


Fig. 3. ORTEP plot (30% probability ellipsoids) for the major rotamer of (1-Me-2-Ph–Ind)Ni(PPh_3)(Thienyl) (**5**). The H atoms and Ph groups of the PPh_3 ligand have been omitted for clarity.

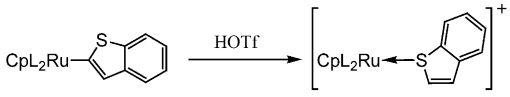
occupancies are ca. 86:14 in **1**, 84:16 in **2**, and 74:26 in **5**; the orientations shown in Figs. 1–3 represent the dominant models.

The Ni center in each of these complexes is within reasonable bonding distance from the P, C11, C1, C2, and C3 atoms, but considerably farther away from C3a and C7a. The extent of Ni–Ind interaction is reflected in the so-called 'slip' parameter $\Delta(M-C) = 1/2\,[(M-C3a + MC7a) - (M-C1 + MC3)]$, [9] which is ca. 0.21 Å for the three complexes studied here. These $\Delta(M-C)$ values and the fold and hinge angles (FA, HA, as defined in Table 3) indicate an intermediate ($\eta^5 \leftrightarrow \eta^3$) hapticity for the Ind ligands in **1**, **2**, and **5** [10]. Comparison of the Ni–C1 and Ni–C3 distances with each other and to the corresponding values in the analogous complexes (Ind)Ni(PPh_3)(X) implies that the trans influences of the ligands X follow the order $PPh_3 \approx$ Me [3] > thienyl ≈ CC–Ph [2] > SPh [11] > phthalimide [12] ≈ Cl^- [3].

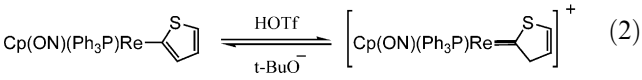
Although the disordered thienyl ligands reduce the accuracy of the Ni–C11 bond lengths, the values obtained (1.91–1.92 Å for the major rotamers in **1**, **3** and **5**) are reliable enough to allow a meaningful comparison with the corresponding Ni–C distances in the Ni–Me (ca. 1.99 Å)[3] and Ni–CC–Ph (ca. 1.86 Å) [2] analogues. Therefore, these structural data support the notion that M–C bond strengths increase with increasing s-character of the C atom.

2.2. Protonation of thienyl complexes with CF_3SO_3H

Protonation of M–alkyl complexes with Brønsted acids HX normally results in the formation of the corresponding M–X and R–H products (i.e. protonation at the α-C), whereas M–alkenyl and alkynyl complexes can give either this type of reaction or conversion to the corresponding M–carbene [13] or M–vinylidene [14] products, respectively (i.e. protonation at the β-C). The factors governing the regiochemistry of these protonations (or electrophilic attacks) are not well understood and the precise outcome of each reaction seems to depend on the electronic nature of the metallic center, the electronic properties of the ancillary ligands, and the source of acid (or electrophile) [15]. In the case of a series of Ru–benzothienyl and Re–thienyl complexes, Angelici et al. have shown that protonation can occur at either the α- or the β-C of the thienyl ligand to give $\eta^1(S)$-thiophene (Eq. (1)) or thienylcarbene (Eq. (2)) complexes, respectively [6,16]. We were interested in converting the Ni–thienyl complexes **1**–**5** to their analogous cationic carbene derivatives, but experiments showed that the protonation reactions take place at the α-C only, as described below.



(1)



(2)

Reacting the compounds **1**–**5** with one equivalent of $HBF_4 \cdot Et_2O$ led to the decomposition of the starting materials and gave $[HPPh_3]^+$ as the only identifiable product ($^{31}P\{^1H\}$-NMR: ca. 5 ppm). When $HBF_4 \cdot H_2O$ was used instead, the starting materials were converted to their corresponding bis(phosphine) cations, [IndNi(PPh_3)$_2$][BF_4], identified on the basis of their characteristic $^{31}P\{^1H\}$-NMR spectra (e.g. for the reaction of **1** ($CDCl_3$): 35.8 (d, $^2J_{P-P} = 25$), 32.5 (d, $^2J_{P-P} = 25$)) [17]. The latter presumably arise from the protonation of the thienyl moiety at the α-C to generate the unstable species $[IndNi(PPh_3)]^+$, which is known [17] to give the bis(phosphine) cations (Scheme 2).

Table 1
Data collection and refinement parameters for complexes **1**, **2**, **5** and **9**

	1	**2**	**5**	**9**
Formula	$C_{32}H_{27}NiPS$	$C_{33}H_{29}NiPS$	$C_{38}H_{31}NiPS$	$C_{35}H_{28}F_3NiO_3PS$
Molecular weight	533.276	547.302	609.368	675.314
Crystal color	Red–orange	Red	Dark brown	Dark red
Crystal habit	Block	Block	Block	Block
Crystal dimensions (mm)	0.63 × 0.46 × 0.21	0.35 × 0.30 × 0.08	0.72 × 0.36 × 0.21	0.43 × 0.30 × 0.12
Cell setting	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pbca*	*Pbca*	$P2_1/n$	*Pbca*
a (Å)	17.1552(1)	17.127(8)	10.6902(1)	10.1641(1)
b (Å)	16.4950(1)	16.716(9)	15.1392(1)	17.3104(1)
c (Å)	18.3638(1)	19.160(5)	19.6099(1)	36.0549(1)
β (°)			104.348(1)	
V (Å^3)	5196.50(5)	5485(4)	3047.70(4)	6343.67(7)
Z	8	8	4	8
D_{calc} (g cm^{-3})	1.3633	1.3254	1.3164	1.4142
λ (Cu–K$_\alpha$) (cm^{-1})	1.54178	1.54056	1.54178	1.54178
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Diffractometer	Bruker AXS	Nonius CAD-4	Bruker AXS	Bruker AXS
$2\theta_{max}$ (°)	145.64	139.64	145.78	145.64
Data collection method	ω scan	ω–2θ scan	ω scan	ω scan
Number of reflections used ($I > 2\sigma(I)$)	4757	2559	5648	4962
R, R_w	0.0365, 0.0977	0.0407, 0.0831	0.0391, 0.1132	0.0634, 0.1938

Table 2
Selected bond distances (Å) for **1**, **2**, **5** and **9** [a]

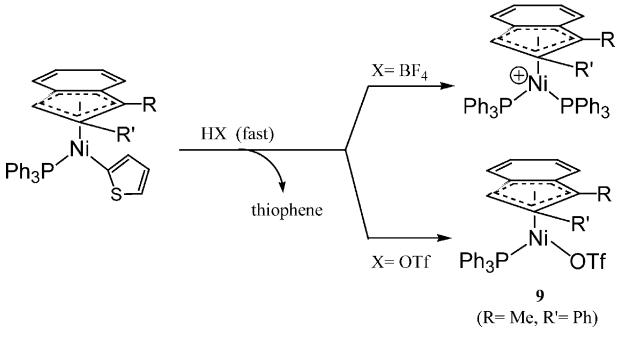
	1	**2**	**5**	**9**
Ni–C11(O1)	1.912(3)	1.921(4)	1.909(3)	1.972 (9)
Ni–P	2.1541(5)	2.1551(11)	2.1490(5)	2.2024(8)
Ni–C1	2.1058(17)	2.083(3)	2.0914(17)	2.171(3)
Ni–C2	2.0742(17)	2.073(3)	2.0853(16)	2.076(3)
Ni–C3	2.0709(18)	2.088(3)	2.0698(17)	2.018(3)
Ni–C3a	2.3066(17)	2.303(3)	2.2894(17)	2.313(4)
Ni–C7a	2.2924(17)	2.279(3)	2.2853(18)	2.360(3)
C1–C2	1.416(3)	1.412(4)	1.424(3)	1.392
C2–C3	1.407(3)	1.410(4)	1.415(3)	1.435(5)
C3–C3a	1.449(3)	1.433(5)	1.450(3)	1.452(5)
C1–C7a	1.455(3)	1.436(4)	1.455(3)	1.479(5)
C3a–C7a	1.427(2)	1.432(4)	1.416(3)	1.404(5)
ΔM–C [b]	0.21	0.21	0.21	0.24

[a] Values given are for the major rotamers only.
[b] $\Delta(M-C) = 1/2[(Ni-C3a+Ni-C7a)-(Ni-C1+Ni-C3)]$.

Table 3
Selected bond angles (°) for **1**, **2**, **5** and **9**

	1	**2**	**5**	**9**
C11(O1)–Ni–P	93.50(12)	96.1(4)	93.4(3)	95.5(7)
C3–Ni–P	104.24(5)	104.05(10)	105.92(6)	98.85(10)
C1–Ni–P	169.41(5)	168.75(10)	167.89(6)	164.0(10)
C11(O1)–Ni–C3	162.19(13)	159.8(4)	160.6(3)	165.7(7)
C3–Ni–C1	66.66(7)	66.50(13)	66.85(8)	65.97(14)
C1–Ni–C11(O1)	95.82(14)	93.5(4)	94.2(3)	99.7(7)
C21–C2–Ni			124.92(13)	
HA*	9.53(0.13)	9.21(0.23)	10.06(0.20)	9.48
FA*	9.46(0.12)	8.44(0.22)	10.84(0.19)	7.57

* HA (hinge angle), angle between the planes defined by C1, C2, C3 and C1, C3, C3a, C7a; FA (fold angle), angle between the planes defined by C1, C2, C3 and C3a, C4, C5, C6, C7, C7a.



Scheme 2.

Protonating the Ni–thienyl complexes with triflic acid, CF_3SO_3H·(HOTf), caused an immediate color change from dark-yellow to red. Analysis by NMR indicated that the reaction mixtures contained free thiophene, [18] small amounts of $[IndNi(PPh_3)_2]^+$, and the new derivatives (R–Ind)(PPh_3)Ni–OTf displaying $^{31}P\{^1H\}$ resonances at ca. 30 ppm (Scheme 2). On the other hand, reacting **1**–**5** with $CF_3SO_3CH_3$ led to a slow conversion of the Ni–thienyl precursors to a mixture of products arising from the addition of Me^+ at (1) PPh_3 to give [$PMePh_3$][OTf], which was identified by its $^{31}P\{^1H\}$ signal at 22.13 ppm, and at (2) the α-C of the Ni–thienyl moiety to give 2-Me–thiophene and the corresponding Ni–OTf (major) and the bis(PPh_3) cations (minor).

We conclude, therefore, that the primary site of protonation (or electrophilic attack) in the complexes **1**–**5** is at the α-C of the Ni–thienyl moiety. In principle, this reaction should lead, initially, to the formation of sulfur-bound $\eta^1(S)$-thiophene compounds, [6] but intermediates of the type $[Ind(PPh_3)Ni(\eta^1(S)\text{-thiophene})]^+[OSO_2CF_3]^-$ were never detected in our studies. Indeed, NMR experiments showed that thiophene does not displace the OTf ligand in the new Ni–OTf products; furthermore, our attempts to generate cationic Ni–($\eta^1(S)$-thiophene) complexes directly from the Ni–Cl precursors have given the bis(PPh_3) cations instead. These results imply that even if protonation of the Ni–thienyl compounds gave Ni-($\eta^1(S)$-thiophene) intermediates initially, they would rearrange rapidly to give the more stable Ni–OTf analogues.

Owing to the poor nucleophilicity of the triflate ligand, M–triflate complexes can act as precursors to highly reactive cationic intermediates. For example, lanthanide triflates [19] and complexes such as $L_2Ti(OTf)_2$ (L = various combinations of elaborated Cp–Ind ligands) [20] act as powerful Lewis acids in organic synthesis, while $Cp^*(PMe_3)(Me)Ir(OTf)$ activates C–H bonds of alkanes [21]. Mindful of these potential reactivities, we sought to isolate and completely characterize the Ni–OTf derivatives produced by the protonation of the Ni–thienyl complexes. Thus, (1-Bz–Ind)Ni(PPh_3)(OSO_2CF_3) (**9**) was isolated from the reaction of **4** with one equivalent of CF_3SO_3H in CH_2Cl_2 and purified by recrystallization from CH_2Cl_2–hexane. The ^{1}H-NMR spectrum of **9** displayed a mutiplet at 3.00 ppm due to H3, two doublets of doublets at 3.62 ppm ($^2J_{H-H}$ = 16.6 Hz, $^4J_{P-H}$ = 4.8 Hz) attributed to the diastereotopic benzyl protons, and two doublets at 5.90 (H4) and 6.09 ppm (H2). In addition, we observed a $^{31}P\{^1H\}$ signal at 29.7 ppm (PPh_3) and an $^{19}F\{^1H\}$ signal at −79.6 ppm ($CF_3SO_3^-$); the latter is comparable with the signal at ca. −78 ppm for the triflate moiety in *trans*-[Ni(OTf)(2-C_5F_4N)(PEt_3)$_2$] [22].

2.3. Solid-state structure of 9

An X-ray diffraction study was carried out on single crystals obtained from the slow evaporation of toluene solutions of **9** at room temperature. This study showed that the OTf moiety exhibits a four-fold orientational disorder; Fig. 4 depicts an ORTEP diagram for the major component of **9**. The triflate ligand is bonded in an η^1(O) fashion to the nickel center with an average Ni–O distance of 1.955 Å, which is longer than the Ni–O distance of ca. 1.89 Å in $Cp^*(PEt_3)Ni(OR)$ (R = *p*-MeC_6H_4, Me); a similar relationship has been observed between the Ni–O bond distances in *trans*-[Ni(X)(2-C_5F_4N)(PEt_3)$_2$]: 1.957(2) Å for X = OTf versus 1.894(4) Å for X = Oph [22].

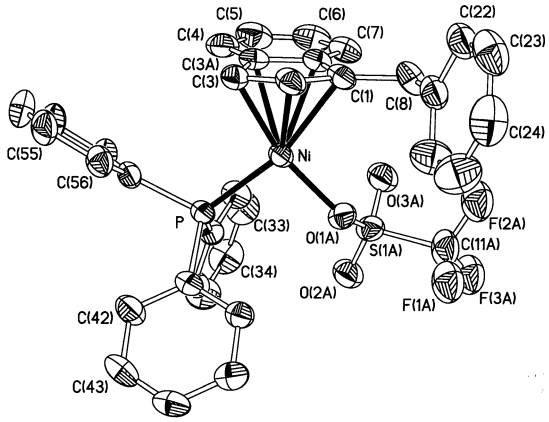


Fig. 4. ORTEP plot (30% probability ellipsoids) for the major rotamer of (1-Bz–Ind)Ni(PPh_3)(OTf) (**9**). The H atoms have been omitted for clarity.

The overall geometry around the Ni center in **9** is very similar to those of the thienyl complexes discussed above, but a number of subtle differences can be observed. For instance, the Ind ligand is more 'tilted' and 'slipped' in **9** compared with the thienyl derivatives: (Ni–C1)–(Ni–C3) = 0.15 Å in **9** versus 0.01–0.04 Å in **1**, **2**, and **5**; ΔM–C = 0.24 in **9** versus 0.21 Å in **1**, **2**, and **5**. We have noted previously that such differences in the coordination mode of Ind are due to the poorer nucleophilicity and smaller *trans* influence of the X ligands such as Cl [3] and phthalimidate [12] compared with better σ-donors such as CC–Ph [2] and Me [3]. Another important structural difference between the Ni–OTf and Ni–CR_n complexes is the Ni–P distance, which is 2.20 Å in **9** versus ca. 2.15 Å in **1**, **2**, and **5** and 2.12 Å in the corresponding Ni–Me [3] analogue. This might be ascribed to the mismatch between PPh_3, a relatively soft Lewis base, and the Ni center, which is a harder Lewis acid when it is bonded to ligands such as OTf versus C-based ligands such as alkynyl, thienyl, Me, etc. [23].

2.4. Catalytic effectiveness of the thienyl complexes in the polymerization of PhCCH

Recent work in our group has shown that mixtures of MAO and (1-Me–Ind)Ni(PR_3)(X) (X = Me, generated in-situ from the Ni–Cl precursor, and CCPh) catalyze the polymerization of phenylacetylene to *cis*-transoidal poly(phenylacetylene) ($M_w = 2–6 \times 10^4$ Da, M_w/M_n = 1–3). In order to probe the influence of the ligand X on this reaction, we studied the catalytic polymerization of phenylacetylene using the analogous Ni–thienyl complexes as pre-catalysts under similar reaction conditions (ten equivalents of MAO, 60 equivalents of Ph–CC–H, THF, room temperature, 24 h). These reactions gave the expected *cis*-transoidal poly(phenylacetylene) on the basis of their NMR spectra; GPC analyses

showed that these samples consisted of somewhat longer chains ($M_w = 5.0–7.5 \times 10^4$ Da) of much poorer monodispersities ($M_w/M_n = 3.7–5.8$) compared with the polymers obtained from the Ni–CCPh reactions ($M_w \sim 5.0 \times 10^4$ Da and $M_w/M_n \sim 1.3$).

No optimization studies have been carried out for the polymerization reactions involving the Ni–thienyl precatalysts, but NMR experiments have indicated that these reactions follow a mechanism similar to those catalyzed by the Ni–CCPh precursors. Thus, a small excess of MAO converts **1** to species displaying the characteristic $^{31}P\{^1H\}$- and ^1H-NMR signals for the corresponding Ni–Me analogue [3], with little or no trace of the corresponding cations; addition of Ph–CC–H to this sample initiated the polymerization. In analogy with our previous reports, we believe that the Ni–thienyl complexes are in rapid equilibrium with their Ni–Me counterparts through bimetallic intermediates bearing a Ni(μ-thienyl)(μ-Me)Al core. The relatively weakened Ni–R moieties in the latter species facilitate the insertion of the Ph–CC–H. It is not clear yet whether the Ind ligands undergo slippage during these steps, but the analogoues Cp complexes are significantly less reactive in this type of reaction [24].

3. Summary

The structural studies of complexes **1**, **2**, and **5** have shown no major difference in the structures of these complexes as a function of the different Ind substituents. The Ni–C bond lengths in the thienyl complexes were found to be intermediate between those of the Ni–Me and Ni–CC–Ph analogues. A brief examination of the polymerization of phenylacetylene catalyzed by the thienyl complexes has affirmed the importance of the character of the Ni–X bond in the precursor for their reactivities: Ni–CCPh and Ni–thienyl precursors give higher activities and longer chains than the Ni–Cl–Ni–Me precursors.

Protonating the Ni–thienyl complexes with CF_3SO_3H generated the corresponding Ni–OTf compounds instead of the desired cationic thienyl carbene derivatives. The solid structure of one of these complexes has revealed relatively long Ni–P and Ni–O distances. Future studies will examine the reactivities of the Ni–OTf derivatives in ligand substitution and polymerization reactions.

4. Experimental

All manipulations and experiments were performed under an inert atmosphere using standard Schlenk techniques and/or in a nitrogen-filled glovebox. Dry, oxygen-free solvents were employed throughout. Bruker AMX400 and AV300 spectrometers were employed for recording ^1H- (400 and 300 MHz), $^{13}C\{^1H\}$- (100.56 and 75.42 MHz), ^{19}F- (376.31 MHz), and $^{31}P\{^1H\}$- (161.92 MHz) NMR spectra at ambient temperature. The NMR spectra are referenced to solvent resonances (^1H- and $^{13}C\{^1H\}$-), 85% H_3PO_4 (0 ppm in $^{31}P\{^1H\}$-), and $C_6H_5CF_3$ (−63.9 ppm in ^{19}F-). The elemental analyses were performed by Laboratoire d'Analyse Elémentaire (Université de Montréal). The molecular weights of the poly(phenylacetylene) were determined on a Waters 510 liquid chromatograph equipped with μ-styragel columns and a Waters 410 differential diffractometer. The precursors (1-R–Ind)$NiPPh_3Cl$ (R = Me, Et, *i*Pr, and Bz) and (1-Me-2-Ph–Ind)$NiPPh_3Cl$ were prepared as described elsewhere; [25] 2-thienylithium was prepared by the deprotonation of thiophene with BuLi. The compounds MAO, PhCCH, thiophene, and CF_3SO_3H were purchased from Aldrich and used as received.

4.1. Synthesis of (1-Me–Ind)Ni(PPh_3)(thienyl) (1)

A stirred benzene solution (25 ml) of 2-thienylithium (1.10 ml of a 1.0 M solution in THF, 1.10 mmol) was added dropwise to a stirred benzene solution (15 ml) of (1-Me–Ind)Ni(PPh_3)Cl (**6**) (360 mg, 0.74 mmol). The resulting orange mixture was stirred for 10 min at room temperature (r.t.), filtered, and the filtrate was evaporated. The orange, oily residue was triturated in 20 ml of EtOH at r.t. to give the product as a dark yellow powder (230 mg, 58%). Recrystallization of **1** from a benzene–EtOH mixture gave single crystals suitable for X-ray analysis. ^1H-NMR (C_6D_6, 400 MHz): 1.44 (s, IndCH_3), 4.05 (br s, H3), 6.27 (d, $J_{H-H} = 2.6$), 6.39 (s, H2), 6.53 (d, $J_{H-H} = 2.4$), 6.97–7.41 (m, ArH), 7.42 (d, $J = 4.7$). ^1H-NMR (acetone-d_6, 300 MHz): 1.26 (d, $^3J_{P-H} = 2.6$, Ind–CH_3), 4.09 (br s, H3), 6.09 (d, $^3J_{H-H} = 2.0$, H12), 6.37 (br s, H4), 6.47 (d, $^3J_{H-H} = 2.3$, H2), 6.67 (pseudo t, $^3J_{H-H} = 3.5$, H13), 6.99–7.42 (m, Aromatic H), 7.02 (t, $^3J_{H-H} = 7.6$, H6); the signals for the remaining protons were not observed and are presumably obscured by the aromatic resonances. $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100.56 MHz): 11.51 (Ind–CH_3), 74.64 (C3), 94.90 (br, C1), 102.70 (C2), 116.90 (C3a), 117.24 (C7a), 121.32 (C13 or C14), 122.24 (br, C12), 123.48, 124.16, 126.89 (C13 or C14), 127.79 (d, $^3J_{P-C} = 10.4$, *m*-*C* of PPh_3), 128.27 (*p*-*C* of PPh_3), 129.54, 129.66, 132.90 (d, $^1J_{P-C} = 43.7$, *i*-*C* of PPh3), 133.64 (d, $^2J_{P-C} = 11.1$, *o*-*C* of PPh3), 139.93(br, C11). $^{31}P\{^1H\}$-NMR (C_6D_6): 37.26 (s). Anal. Calc. for $C_{29}H_{24}PNiS$: C, 72.07; H, 5.10; S, 6.01. Found: C, 71.95; H, 5.19; S, 5.88%.

4.2. Synthesis of (1-Et–Ind)Ni(PPh_3)(thienyl) (2)

Complex **2** was prepared in the same manner as **1** using 2-thienylithium (0.60 ml of a 1.0 M solution in THF, 0.60 mmol) and (1-Et–Ind)Ni(PPh_3)Cl (**7**) (198

mg, 0.4 mmol) to give the Ni–thienyl product as a brown powder (160 mg, 74%). Red, X-ray quality crystals were obtained upon cooling (−20 °C) the filtrate obtained from the extraction of the brown powder into EtOH. ^{1}H-NMR (C_6D_6, 400 MHz): 1.10 (t, $^3J_{H-H} = 7.3$, IndCH$_2$CH_3), 1.90 (br, IndCH_2), 4.07 (br s, H3), 6.35 (d, $J_{H-H} = 2.6$), 6.46 and 6.54 (d, $J_{H-H} = 1.9$), 7.40 (d, $J_{H-H} = 4.7$), 6.97–7.40 (m, ArH). ^{1}H-NMR (acetone-d_6, 300 MHz): 1.07 (t, $^3J_{H-H} = 7.6$, Ind–CH$_2$CH_3), 1.66 (m, Ind–CH$_2$), 4.07 (br s, H3), 6.09 (d, $^3J_{H-H} = 2.3$, H12), 6.44 (br s, H4), 6.53 (d, $^3J_{H-H} = 2.8$, H2), 6.66 (pseudo t, $^3J_{H-H} = 3.5$, H13), 7.02 (t, $^3J_{H-H} = 7.6$, H6), 7.16–7.72 (m, Aromatic H); the signals for the remaining protons were not observed and are presumably obscured by the aromatic resonances. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.56 MHz): 12.44 (Ind–CH$_2$*C*H$_3$), 19.37 (Ind–*C*H$_2$), 74.74 (C3), 100.73 (C2), 117.10 (C3a), 117.33 (C7a), 121.40 (br, C12), 121.76 (C13 or C14), 123.51, 124.09, 126.82, 127.76 (d, $^3J_{P-C} = 9.7$, *m*-*C* of PPh$_3$), 129.35 (C13 or C14), 129.64 (*p*-*C* of PPh$_3$), 132.95 (d, $^1J_{P-C} = 43.6$, *i*-*C* of PPh3), 133.61 (d, $^2J_{P-C} = 11.1$, *o*-*C* of PPh3), 138.95 (br, C11). ^{13}C{^{1}H}-NMR (C_6D_6, 100.56 MHz): 13.19 (Ind–*C*H$_2$*C*H$_3$), 20.44 (Ind–*C*H$_2$), 75.74 (C3), 101.55 (C2), 109.54 (C1), 122.61 and 122.96 (C3a and C7a), 124.50, 125.09, 128.11 (d, $^3J_{P-C} = 2.7$, C12), 128.62 (*m*-*C* of PPh$_3$), 130.36 (d, $^2J_{P-C} = 2.8$, *p*-C of PPh$_3$), 130.91 (br, C13 or C14), 134. 12 (d, $J_{P-C} = 42.6$, *i*-*C* of PPh3), 134.44 (d, $^3J_{P-C} = 11.0$, *o*-*C* of PPh$_3$), 134.86 (br, C11). ^{31}P{^{1}H}-NMR (C_6D_6): 37.11 (s). Anal. Calc. for $C_{30}H_{26}PNiS$: C, 72.42; H, 5.34; S, 5.86. Found: C, 72.14; H, 5.27; S, 5.81%.

4.3. Synthesis of (1-iPr–Ind)Ni(PPh$_3$)(thienyl) (3)

Complex **3** was prepared in the same manner as 1 using 2-thienylithium (2.20 ml of a 0.66 M solution in THF, 1.46 mmol) and (1-*i*-Pr–Ind)Ni(PPh$_3$)Cl (8) (500 mg, 0.97 mmol) to give the product as a brown powder (400 mg, 73%). Extraction into EtOH, followed by filtration and cooling gave analytically pure material. ^{1}H-NMR (C_6D_6, 400 MHz): 1.10 and 1.25 (d, $^3J_{H-H} = 6.2$ and 6.9, IndCH(CH_3)$_2$), 2.36 (br s, IndCH(CH$_3$)$_2$), 4.02 (br s, H3), 6.32 (d, $J_{H-H} = 3.0$), 6.52 (d, $J_{H-H} = 2.7$), 7.08 (t, $J_{H-H} = 7.3$), 7.26–7.55 (ArH). ^{1}H-NMR (acetone-d_6, 400 MHz): 1.10 (d, $^3J_{H-H} = 6.6$, Ind–CH(CH_3)$_2$), 4.02 (br s, H3), 6.09 (d, $^3J_{H-H} = 3.2$, H12), 6.50 (d, $^3J_{H-H} = 3.2$, H2), 6.57 (br, H4), 6.63 (dd, $^3J_{H-H} = 4.8$ and 3.2, H13), 7.03 (t, $^3J_{H-H} = 8.0$, H6), 7.09 (d, $^3J_{H-H} = 4.8$, H14), 7.27–7.55 (m, Aromatic H); the signals for the remaining protons were not observed and are presumably obscured by the aromatic resonances. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.56 MHz): 20.55 and 22.16 (CH(*C*H$_3$)$_2$), 25.08 (*C*H(CH$_3$)$_2$), 74.60 (br, C3), 98.45 (C2), 105.29 (br, C1), 117.28 (C3a), 118.02 (C7a), 120.53 and 121.95 (C13 and C14), 123.84, 126.83, 127.83 (d, $^3J_{P-C} = 9.7$, *m*-*C* of PPh$_3$), 128.32, 129.01, 129.71 (*p*-*C* of PPh$_3$), 133.14 (d, $^1J_{P-C} = 44.4$ Hz, *i*-*C* of PPh3), 133.70 (d, $^2J_{P-C} = 11.1$ Hz, *o*-*C*–PPh3), 134.06, 138.20 (br, C11). ^{31}P{^{1}H}-NMR (C_6D_6): 37.42 (s). Anal. Calc. for $C_{34}H_{31}PNiS$: C, 72.75; H, 5.57; S, 5.71. Found: C, 72.31; H, 5.59; S, 6.28%.

4.4. Synthesis of (1-Bz–Ind)Ni(PPh$_3$)(thienyl) (4)

Complex **4** was prepared in the same manner as **1** using 2-thienylithium (1.78 ml of a 1.0 M solution in THF, 1.78 mmol) and (1-Bz–Ind)Ni(PPh$_3$)Cl (**9**) (500 mg, 0.89 mmol) to give the product as a brown powder (414 mg, 77%). Extraction into EtOH, followed by filtration and cooling gave analytically pure material. ^{1}H-NMR (400 MHz, C_6D_6): 3.24 and 3.27 (br s, IndCH_2), 4.05 (br s, H3), 6.31 (br s), 6.44 (br s), 6.60 (br s), 6.97–7.44 (ArH). ^{1}H-NMR (acetone-d_6, 300 MHz): 2.91 and 3.08 (d, $^2J_{H-H} = 14.5$, Ind–CH$_2$), 4.11 (br s, H3), 6.17 (d, $^3J_{H-H} = 1.9$, H12), 6.43 (br s, H4), 6.56 (d, $^3J_{H-H} = 2.9$, H2), 6.73 (dd, $^3J_{H-H} = 4.5$ and 3.5, H13), 7.02 (t, $^3J_{H-H} = 7.0$, H6), 7.18–7.69 (m, Aromatic H); the signals for the remaining protons were not observed and are presumably obscured by the aromatic resonances. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.56 MHz): 32.69 (*C*H$_2$–Ph), 75.45 (C3), 97.13 (br, C1), 102.37 (C2), 117.17 and 117.49 (C3a and C7a), 121.53, 121.61, 123.68, 124.13, 125.73, 127.04, 127.77 (d, $^3J_{P-C} = 9.7$, *m*-*C* of PPh$_3$), 128.65, 129.69 (*p*-*C* of PPh$_3$), 133.06 (d, $^1J_{P-C} = 43.7$, *i*-*C* of PPh3), 133.59 (d, $^2J_{P-C} = 11.1$, *o*-*C* of PPh3), 133.99, 138.40 (br, C11), 139.70. ^{31}P{^{1}H}-NMR (C_6D_6): 37.11 (s). Anal. Calc. for $C_{38}H_{31}PNiS$: C, 74.90; H, 5.13; S, 5.26. Found: C, 74.29; H, 5.16; S, 5.08%.

4.5. Synthesis of (1-Me-2-Ph) Ni(PPh$_3$)(thienyl) (5)

Complex **5** was prepared in the same manner as **1** using 2-thienylithium (1.82 ml of a 0.66 M solution in THF, 1.20 mmol) and (1-Me-2-Ph–Ind)Ni(PPh$_3$)Cl (10) (450 mg, 0.80 mmol) to give the product as a brown powder (380 mg, 76%). Crystals of **5** suitable for X-ray crystallorgraphy were obtained by recrystallization from a THF–toluene mixture at r.t. ^{1}H-NMR (C_6D_6, 400 MHz): 1.58 (d, $^4J_{P-H} = 4.5$, IndCH_3), 4.32 (d, $^3J_{P-H} = 3.0$, H3), 6.51 (d, $J_{H-H} = 7.8$), 6.57 (d, $J_{H-H} = 3.3$), 7.77 (d, $J_{H-H} = 1.1$), 7.79 (d, $J_{H-H} = 1.4$). ^{1}H-NMR (acetone-d_6, 300 MHz): 1.38 (d, $^4J_{P-H} = 4.5$, Ind–CH_3), 4.28 (d, $^3J_{P-H} = 3.1$, H3), 6.11 (d, $^3J_{H-H} = 2.9$, H12), 6.45 (d, $^3J_{H-H} = 7.9$, H4), 6.69 (dd, $^3J_{H-H} = 4.7$ and 3.4, H13), 7.07–7.73 (m, Aromatic H); the signals for the remaining protons were not observed and are presumably obscured by the aromatic resonances. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.56 MHz): 10.23 (*C*H$_3$–Ind), 74.58 (C3), 91.47 (d, $J = 13.19$, C1), 116.48, 117.53, 120.50 (d, $J =$

7.6, C12), 122.87, 123.78, 129.37, 129.70, 124.35, 127.02, 127.19, 127.84 (d, $^3J_{P-C} = 9.7$, *m-C* of PPh_3), 128.39 (*p-C* of PPh_3), 128.32, 129.01,129.19, 132.91 (d, $^1J_{P-C} = 43.7$, *i-C* of PPh3), 133.27, 133.64 (d, $^2J_{P-C} = 11.1$, *o-C* of PPh3), 135.94, 141.28 (d, $^2J_{P-C} = 28.4$, C11). $^{31}P\{^1H\}$-NMR (C_6D_6): 37.36 (s). Anal. Calc. for $C_{38}H_{31}PNiS$: C, 74.90; H, 5.13; S, 5.26. Found: C, 73.71; H, 5.16; S, 5.18%.

4.6. General procedure for the reaction of complexes 1–5 with one equivalent of CF_3SO_3H

A 5 mm NMR tube was charged with the Ni–thienyl complex and 0.55 ml of C_6D_6. One equivalent of CF_3SO_3H was added to the solution and the tube was shaken, resulting in an immediate color change (brown to red). The ^1H- and $^{31}P\{^1H\}$-NMR spectra of the sample showed a nearly quantitative conversion to the Ni–OTf derivative (**6**–**10**) in all cases.

4.7. Reaction of 1 with CF_3SO_3H

The general procedure outlined above was used for the reaction of **1** (15 mg, 0.028 mmol) with CF_3SO_3H (2.5 μl, 0.028 mmol) to give (1-Me–Ind)Ni(PPh_3)(OTf) (**6**). ^1H-NMR (C_6D_6, 400 MHz): 1.44 (d, $^4J_{P-C} = 5.9$ Hz, –C*H*$_3$–Ind), 3.04(br s, H3), 5.70(d, $^3J_{H-H} = 6.4$ Hz, H4), 6.16 (s, H2), 6.74 (t, $^3J_{H-H} = 7.4$ Hz, H5), 6.90 (t, $^3J_{H-H} = 7.8$ Hz, H6), 7.00(m, ArH), 7.33 (d, $^3J_{H-H} = 7.4$, H7) (m, ArH). $^{31}P\{^1H\}$-NMR (C_6D_6): 30.25 (s).

4.8. Reaction of 2 with CF_3SO_3H

The general procedure outlined above was used for the reaction of **2** (15 mg, 0.027 mmol) with CF_3SO_3H (2.4 μl, 0.027 mmol) to give (1-Et–Ind)Ni(PPh_3)(OTf) (**7**). ^1H-NMR (C_6D_6, 400 MHz): 1.29 (t, $^3J_{H-H} = 7.3$ Hz, –C*H*$_3$), 1.74 and 2.27 (m, –C*H*$_2$), 3.04 (s, H3), 5.80 (d, $^3J_{H-H} = 6.8$ Hz, H4), 6.21 (d, $^3J_{H-H} = 2.6$ Hz, H2), 6.75 (t, $^3J_{H-H} = 7.0$ Hz, H5), 7.08 (t, $^3J_{H-H} = 7.4$ Hz, H6), 7.00 (m, ArH), 7.38 (d, $^3J_{H-H} = 8.0$ Hz, H4), 7.51 (m, ArH). $^{31}P\{^1H\}$-NMR (C_6D_6): 30.02 (s). $^{19}F\{^1H\}$-NMR(C_6D_6): −79.70 (s).

4.9. Reaction of 3 with CF_3SO_3H

The general procedure outlined above was used for the reaction of **3** (15 mg, 0.027 mmol) with CF_3SO_3H (2.4 μl, 0.027 mmol) to give (1-*i*-Pr–Ind)Ni(PPh_3)(OTf) (**8**). ^1H-NMR (C_6D_6, 400 MHz): 1.56 (d, $^3J_{H-H} = 6.5$ Hz, CH(C*H*$_3$)$_2$), 1.14 (d, $^3J_{H-H} = 7.0$ Hz, CH(C*H*$_3$)$_2$), 2.93 (m, C*H*(CH$_3$)$_2$), 3.02 (dd, $^3J_{H-H} = 2.6$ Hz, $^3J_{P-H} = 4.8$ Hz, H3), 6.06 (d, $^3J_{H-H} = 7.8$ Hz, H4), 6.14 (d, $^3J_{H-H} = 2.6$ Hz, H2), 6.79 (t, $^3J_{H-H} = 7.9$ Hz, H5), 7.18 (s, ArH), 7.01 (m, ArH), 7.51 (m, ArH). $^{31}P\{^1H\}$-NMR (C_6D_6): 29.30 (s). $^{19}F\{^1H\}$-NMR (C_6D_6): −79.79 (s).

4.10. Reaction of 5 with CF_3SO_3H

The general procedure outlined above was used for the reaction of **5** (16 mg, 0.026 mmol) with CF_3SO_3H (2.4 μl, 0.026 mmol) to give (1-Me-2-Ph)Ni(PPh_3)(OTf) (**10**). ^1H-NMR (C_6D_6): 1.60 (d, $^3J_{P-H} = 6.3$ Hz, Ind–C*H*$_3$), 3.36 (d, $^3J_{P-H} = 5.1$ Hz, H3), 5.96 (d, $^3J_{H-H} = 7.4$Hz, H4), 6.79–7.96 (m, ArH). $^{31}P\{^1H\}$-NMR (C_6D_6): 30.63 (s).

4.11. Synthesis of (1-Bz–Ind)Ni(PPh_3)(OTf) (9)

A CH_2Cl_2 solution (10 ml) of CF_3SO_3H (32 μl, 0.36 mmol) was added dropwise to the stirred CH_2Cl_2 solution (20 ml) of (1-Bz–Ind)Ni(PPh_3)(thienyl) (220 mg, 0.36 mmol) at r.t. The resulting red mixture was stirred for 30 min, filtered, and the filtrate was evaporated to dryness. The residue was crystallized from CH_2Cl_2–hexane at r.t. to give the product as a red powder (110 mg, 46%). Crystals suitable for X-ray diffraction studies were grown by the slow evaporation of a toluene solution at r.t. ^1H-NMR (C_6D_6, 400 MHz): 3.00 (m, H3), 3.62 and 3.34 (dd, $^2J_{H-H} = 16.6$ Hz, $^4J_{P-H} = 4.8$ Hz, –C*H*$_2$–Ph), 5.90 (d, $^3J_{H-H} = 7.4$ Hz, H4), 6.09 (d, $^3J_{H-H} = 1.8$ Hz, H2), 6.74 (t, $^3J_{H-H} = 7.9$ Hz, H5), 7.00 (s, ArH), 7.08 (m, ArH), 7.42 (d, $^3J_{H-H} = 6.6$ Hz, H7), 7.49 (m, ArH). ^{13}C-NMR ($CDCl_3$, 300 MHz): 33.29 (s, *C*H$_2$–Ph), 61.01 (s, C3), 104.41 (s, C2), 110.24, (d, $^2J_{P-C} = 11.3$ Hz, C1), 117.96, 120.06, 126.57, 127.32, 127.76, 128.67 (d, $^3J_{P-C} = 10.8$ Hz, *m*-PPh_3), 129.17, 129.76 (d, $^1J_{P-C} = 44.7$ Hz, *i*-PPh_3), 130.83 (s, *p*-PPh_3), 133.86 (d, $^2J_{P-C} = 11.9$ Hz, *o*-PPh_3), 136.98, 139.22. $^{31}P\{^1H\}$-NMR: 29.66 (s) (in C_6D_6), 29.13 (s) ($CDCl_3$). $^{19}F\{^1H\}$-NMR: −79.62 (s) (in C_6D_6), −81.30 (s) (in $CDCl_3$). IR (KBr): 1626 (m), 1495 (m), 1480 (m), 1436 (s), 1385 (m), 1324 (s), 1263 (s), 1234 (s), 1208 (s), 1180 (s), 1121 (m), 1096 (m), 1032 (s), 1017 (s), 747 (s), 724 (w), 695 (s), 635 (s), 542 (m), 530 (s), 510 (s), 495 (s). FABMS (*m/z*): 525 [$M^+ - Otf$]. Anal. Calc. for $C_{35}H_{28}PNiO_3SF_3$: C, 62.25; H, 4.18; S, 4.75. Found: C, 62.81; H, 4.31; S, 4.34%.

4.12. Reaction of 1 with $CF_3SO_3CH_3$

Monitoring the reaction of **1** with a small excess of $CF_3SO_3CH_3$ by ^{31}P-NMR (C_6D_6) spectroscopy showed the slow conversion of **1** to a mixture of [(1-Me–Ind)Ni(PPh_3)$_2$]$^+$ (two d at 35.65 and 33.53 ppm, $^2J_{P-P} = 25$ Hz), (1-Me–Ind)Ni(PPh_3)(CF_3SO_3) (s at 30.20 ppm), and [$PMePh_3$]$^+$ (s at 22.13 ppm).

4.13. General procedure for the polymerization of phenylacetylene

To a THF solution (ca. 1 ml) of the Ni–thienyl pre-catalyst (ca. 40 mg) was added MAO (ten equivalents)

and phenylacetylene (ca. 50–100 equivalents), and the mixture was stirred for 24 h under nitrogen. The polymerization was quenched by adding a mixture of AcOH–MeOH; the resulting yellow solid (ca. 20–30% yield) was washed with hexane and dried in vacuo. ^{1}H-NMR ($CDCl_3$, 400 MHz): 6.94 (m, *m*- and *p*-H), 6.64 (d, $^3J_{H-H} = 6.6$ Hz, *o*-H), 5.85 (s, vinylic H). The molecular weights of the polymers were determined by GPC (THF): for **1**: $M_w = 49\,829$, $M_n = 13\,453$, $M_w/M_n = 3.7$; for **3**: $M_w = 75\,642$, $M_n = 12\,916$, $M_w/M_n = 5.8$.

4.14. Reaction of Ni–thienyl compounds with MAO

Monitoring the reactions of the Ni–thienyl complexes with a ten-fold excess of MAO by ^{1}H- and ^{31}P{^{1}H}-NMR (C_6D_6) showed the quantitative conversion to (1-Me–Ind)Ni(PPh_3)(Me). ^{1}H-NMR: −0.72 (d, $^3J_{P-H} = 5.6$ Hz), 1.89 (d, $^3J_{H-H} = 3.9$ Hz, Ind–CH_3), 4.16 (t, $^3J_{H-H} = 2.8$ Hz, H3), 6.23 (d, $^3J_{H-H} = 2.9$ Hz, H2), 6.47 (d, $^3J_{H-H} = 7.8$ Hz, H4), 6.22–7.31 (m, ArH). ^{31}P{^{1}H}-NMR: 48.05 (s)

4.15. X-ray diffraction studies

The crystal data for complexes **1**, **5**, and **9** were collected on a Bruker AXS SMART 2K diffractometer with graphite-monochromatic Cu–K_α radiation at 293(2) K using SMART [26]. Cell refinement and data reduction were done using SAINT [27]. The data for complex **2** was collected on a Nonius CAD-4 diffractometer with graphite-monochromatic Cu–K_α radiation at 293(2) using CAD-4 software [28]. The refinement of the cell parameters was done with the CAD-4 software while the data reduction used the NRC-2 and NRC-2A packages [29]. All structures were solved by direct methods, using SHELXS-97 [30] and difmap synthesis using SHELXL-96 [31]; the refinements were done on F^2 by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically, while the hydrogens (isotropic) were constrained to the parent atom using a riding model. Two orientations were found for the thienyl group in **1**, **2** and **5**. Each of them was refined anisotropically using restraints (SAME/SADI/EDAP/FLAT/DFIX) in order to improve the model. The occupancy factor for the thienyl groups are: 0.856(2)/0.144(2) for **1**; 0.841(3)/0.159(3) for **2**; and 0.74/0.26 for **5**. The triflate moiety in complex **9** showed a four-fold rotational disorder, which was dealt with as follows. Model A (31% occupancy) was generated by constraining the main bond distances and angles in the OTf moiety to chemically reasonable values. The remaining models (B: 29%; C: 26%; D: 14%) were generated using the values from model A. Full details are given in the supplementary information. Crystal data and experimental details for **1**, **2**, **5**, and **9** are listed in Table 1 and selected bond distances and angles are listed in Tables 2 and 3, respectively.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre (CCDC No.: 182403 for compound **1**; 182404 for compound **2**; 182405 for compound **5**; 182406 for compound **9**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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