Synthesis and Catalytic Evaluation of Ruthenium–Arene Complexes Generated Using Imidazol(in)ium-2-carboxylates and Dithiocarboxylates

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The ability of five imidazol(in)ium-2-carboxylates and dithiocarboxylates bearing cyclohexyl, mesityl, or 2,6-diisopropylphenyl substituents on their nitrogen atoms to act as NHC precursors for in situ catalytic applications was probed in ruthenium-promoted ring-opening metathesis and atom transfer radical polymerizations. Results obtained with 1:2 mixtures of $[RuCl_2(p-cymene)]_2$ and NHC·CO₂ adducts were in line with those reported previously starting from preformed $[RuCl_2(p-cymene)]_2$ not not complexes, whereas the NHC·CS₂ zwitterions were almost completely inactive. To account for this dichotomy, the preparation of preformed ruthenium–arene complexes from $[RuCl_2(p-cymene)]_2$ and NHC·CS₂ inner salts was thoroughly investigated. As expected, imidazo-lium-2-carboxylates lost their CO₂ moiety and afforded $[RuCl_2(p-cymene)(NHC)]$ complexes in high yields, whereas the NHC·CS₂ betaines retained their zwitterionic nature and led to cationic complexes of the $[RuCl(p-cymene)(NHC·CS_2)]PF_6$ type. These stable, 18-electron species are the first examples of well-defined transition-metal complexes bearing chelating NHC·CS₂ ligands. They were characterized by various analytical techniques, and the molecular structure of $[RuCl-(p-cymene)(IMes\cdotCS_2)]PF_6$ was determined by X-ray diffraction analysis.

Introduction

Stable N-heterocyclic carbenes (NHCs) have become ubiquitous ligands in organometallic chemistry and homogeneous catalysis.¹ They have already afforded an impressive range of transition-metal complexes that have found numerous applications in organic synthesis and polymer chemistry.² Currently, the NHCs most commonly encountered are imidazolin-2-ylidene and imidazolidin-2-ylidene derivatives (with or without a formal double bond between C4 and C5, respectively).³ They are usually obtained by deprotonation of the corresponding imidazol(in)ium salts with a strong base (Scheme 1). Due to the high sensitivity of the free carbenes toward oxygen and moisture, this reaction is often carried out in situ. Therefore, imidazol(in)ium salts serve de facto as stable NHC ligand precursors in various catalytic systems.⁴

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An equally important strategy to obtain transition-metal– NHC complexes involves the reaction of an imidazol(in)ium salt with a silver(I) source. The intermediate Ag(I)–NHC complex formed can readily transfer its carbene ligand to another late transition metal via transmetalation, thereby affording the desired final product (Scheme 1).⁵ Although very general, this method is not exempt from failure, and Ag-induced oxidative degradation of imidazolium precursors bearing alkyl groups on C2 may lead to unexpected reactions.⁶ Thus, new synthetic paths that would allow the convenient and efficient delivery of NHC ligands to transition-metal catalytic centers are highly desirable.

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Scheme 1. Formation of Transition-Metal Complexes from Various NHC Precursors



Recently, we^{7,8} and others^{9,10} have shown that imidazol(in)ium-2-carboxylates readily lost their CO₂ moiety upon heating or dissolution and could serve as efficient carbene precursors in organocatalytic processes^{10,11} or for the synthesis of various transition-metal-NHC complexes (Scheme 1).12 We have already taken advantage of this lability to generate active species in the palladium-catalyzed Suzuki-Miyaura crosscoupling of aryl halides with *trans*-2-phenylvinylboronic acid.⁸ In ruthenium-promoted olefin metathesis and cyclopropanation reactions, we have also shown that a 1:2 mixture of $[RuCl_2(p-cymene)]_2$ dimer and IMes \cdot CO₂ displayed the same level of activity as the preformed [RuCl₂(*p*-cymene)(IMes)] complex (IMes is 1,3-dimesitylimidazolin-2-ylidene, p-cymene is 1-isopropyl-4-methylbenzene).⁷ In sharp contrast with these results, preliminary experiments carried out with imidazol-(in)ium-2-dithiocarboxylates indicated that these adducts compared poorly with their NHC·HCl or NHC·CO₂ counterparts for activating palladium(II) acetate in Suzuki-Miyaura reactions.8

In this contribution, we further investigate the ability of NHC·CO₂ and NHC·CS₂ betaines to serve as carbene ligand precursors for transition-metal complexes. Both types of zwitterions were first employed to generate in situ catalytic species in ruthenium-promoted polymerization reactions. To account for the differences of reactivity observed, we also compared the thermal stabilities of imidazol-(in)ium-2-carboxylates and dithiocarboxylates by thermogravimetric analysis. A second part of this work involved the isolation and characterization of ruthenium–arene complexes obtained from various NHC·CX₂ adducts (X=O, S) in order to validate the assumptions derived from the in situ experiments.

Scheme 2. Imidazol(in)ium-2-carboxylates (X = O) and Dithiocarboxylates (X = S) Used in This Work



Results and Discussion

Catalytic Tests. To begin this study, we wanted to compare the ability of NHC·CO₂ and NHC·CS₂ betaines to act as catalyst modifiers toward ruthenium complexes for in situ catalytic applications. Zwitterionic adducts of five representative saturated or unsaturated NHCs bearing mesityl (Mes), 2,6-diisopropylphenyl (Dip), or cyclohexyl (Cy) substituents on their nitrogen atoms were elected as starting materials for these investigations (Scheme 2).

To complement the data obtained previously with NHC· CO₂ adducts,⁷ we first carried out the ring-opening metathesis polymerization (ROMP) of cyclooctene, a standard testreaction used in our laboratory for assessing the metathetical activity of ruthenium–arene complexes.^{13,14} Reactions were carried out in chlorobenzene at 60 °C using a 1:2 mixture of [RuCl₂(*p*-cymene)]₂ dimer and NHC·CS₂ adducts. The monomer-to-ruthenium molar ratio was 250, and an ordinary neon tube placed 10 cm away from the Pyrex reaction flasks complemented the experimental setup. This device ensured a strong, reproducible visible light illumination required to convert saturated ruthenium–(*p*-cymene) complexes bearing NHC ligands into metathetically active species, most likely via total or partial decoordination of the η^6 -arene ligand.^{15,16}

Despite this photochemical activation, no polymers were isolated in the present study, and only oligomers accounted for the low conversions observed (Table 1). These results sharply contrast with those obtained previously with NHC·CO₂ adducts sporting aryl groups on their nitrogen atoms.⁷ Almost quantitative conversions of the starting material and high yields of polyoctenamer were attained within 2 h with

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Table 1. ROMP of Cyclooctene Catalyzed by	Various Ruthenium—NHC Complexes Generated In Situ from [RuCl ₂ (<i>p</i> -cymene)] ₂ and
	Imidazol(in)ium-2-(dithio)carboxylates

	n	[RuCl ₂ (<i>p</i> -cym)] ₂ (1 equiv.) NHC • CX ₂ (2 equiv.) PhCl, 60 °C, 2 h visible light illumination	(man),	
NHC · CS ₂	conversion $(\%)^a$	NHC·CO ₂	conversion $(\%)^{a,b}$	isolated yield $(\%)^b$
ICy.CS ₂	9	ICy · CO ₂	30	0
IMes · CS ₂	10	IMes · CO ₂	100	91
IDip · CS ₂	4	$IDip \cdot CO_2$	79	64
SIMes · CS ₂	14	SIMes · CO ₂	100	85
$SIDip \cdot CS_2^2$	0	$SIDip \cdot CO_2^2$	89	77

^{*a*} Determined by GC using cyclooctane as internal standard. ^{*b*} Data from ref 7.

Table 2. ATRP of MMA Catalyzed by Various Ruthenium– NHC Complexes Generated In Situ from [RuCl₂(*p*-cymene)]₂ and Imidazol(in)ium-2-(dithio)carboxylates

→Br + n	[RuCl ₂ (<i>p</i> -cym)] NHC • CX ₂ (PbCHa 85	2 equiv.) $2 equiv.)$ $3C 16 b$		
EtO ₂ C	CO ₂ Me	C, TOTT EtO ₂ C	CO ₂ Me	
NHC•CX ₂	isolated yield (%)	M_{n}^{a}	$M_{ m w}/M_{ m n}^{\ a}$	
ICy.CS ₂	< 5	b	b	
$IMes \cdot CS_2$	< 5	44 000	1.68	
$ICy \cdot CO_2$	88	145 000	2.06	
IMes · CO ₂	64	25000	1.27	
$IDip \cdot CO_2$	86	31 000	2.01	
SIMes · CO ₂	74	26 000	1.65	

 a Determined by SEC with PMMA calibration. b Oligomeric products.

mesityl- or 2,6-diisopropylphenyl-substituted carbene precursors, whereas the cyclohexyl-bearing imidazolium-2-carboxylate led to a 30% conversion and afforded only soluble oligomers and no high molecular weight polymer (Table 1). The patent superiority of NHCs bearing aryl groups on their nitrogen atoms over 1,3-dialkyl derivatives was already recognized when [RuCl₂(*p*-cymene)(NHC)] complexes, either preformed or generated in situ from imidazol(in)ium chlorides and a base, were investigated in ROMP reactions.¹⁵ Earlier studies had also shown that the C4–C5 double bond in the imidazole ring was not crucial to achieve high catalytic efficiencies.¹⁷

In a second series of experiments, we have investigated the ruthenium-promoted atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) with selected representative carboxylate or dithiocarboxylate adducts bearing alkyl or aryl groups on their nitrogen atoms (Table 2). Ethyl 2-bromo-2-methylpropionate served as initiator, and the reactions were carried out for 16 h in toluene at 85 °C under the exclusion of oxygen. The initial monomer/initiator/ruthenium molar proportions were 800:2:1. Under these conditions, the two imidazolium-2-dithiocarboxylates tested were almost completely inactive. With $ICy \cdot CS_2$ only oligomers were isolated, whereas with IMes · CS₂ a small amount of polymer precipitated. Yet, molecular weight determination by size-exclusion chromatography (SEC) indicated that the initiation efficiency was very low and the polydispersity rather broad. These results sharply contrasted with those





Figure 1. Comparison of the TGA curves for mesityl-substituted NHC \cdot CO₂ and NHC \cdot CS₂ adducts.

obtained with ICy·CO₂ and IMes·CO₂ using the same experimental protocol (Table 2). The former inner salt did not afford a controlled polymerization, but the latter one displayed a satisfactory activity. It is noteworthy that molecular weights and polydispersities reached with the in situ catalytic systems based on these two NHC·CO₂ adducts were in line with those obtained previously with preformed [RuCl₂(*p*-cymene)(NHC)] complexes bearing the ICy or IMes ligand.¹⁸ Further modifications of the carbene moiety were accomplished by replacing the mesityl groups of IMes with diisopropylphenyl substituents in IDip or by removing the heterocyclic C4–C5 double bond in SIMes. Yet, none of these alterations resulted in a better control of the polymerization (Table 2).

Thermogravimetric Analysis. In order to rationalize the large discrepancy observed between NHC·CO₂ and NHC·CS₂ zwitterions in terms of catalytic activity, we probed their thermal stabilities in the solid state by thermogravimetric analysis (TGA). Decomposition profiles shown in Figure 1 for mesityl-substituted derivatives provide graphic evidence for the greater lability of carboxylate inner salts compared to their dithio analogues, even if clean loss of the CX₂ moiety was not detected in this series. Thus, imidazol(in)ium-2-carboxylates are more likely to release carbene ligands when heated to 60 °C (ROMP experiments) or 85 °C (ATRP conditions) in the presence of the [RuCl₂(*p*-cymene)]₂ dimer, a requisite for generating catalytically active species in situ.

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Similar TGA curves were recorded for the cyclohexyl- and 2,6-diisopropylphenyl-based adducts (not shown). As previously noted, the presence or the absence of a heterocyclic C4–C5 double bond did not significantly alter the onset of the degradation process.^{7,19}

Synthesis of Ruthenium-Arene Complexes. Because imidazol(in)ium-2-dithiocarboxylates obviously behaved very differently from the corresponding carboxylate adducts in catalytic systems generated in situ, we have investigated in more detail the formation of preformed ruthenium-arene complexes from these two types of precursors. In a first series of experiments, the $[RuCl_2(p-cymene)]_2$ dimer was refluxed for 2 h in THF with 2 equiv of $ICy \cdot CO_2$, $IMes \cdot CO_2$, or $IDip \cdot CO_2$. A slow stream of argon was applied on top of the condenser to help displace carbon dioxide. After workup and purification by column chromatography, the corresponding $[RuCl_2(p-cymene)(NHC)]$ complexes (1-3) were isolated in ca. 70-90% yields (Scheme 3). These neutral, 18-electron species are well-known catalyst precursors for several ruthenium-mediated organic transformations,14,20 including ROMP¹⁵ and ATRP.¹⁸ Their synthesis from [RuCl₂(*p*-cymene)]2 and free NHCs has already been reported in the literature.²¹⁻²⁴ From a practical point of view, the recourse to NHC \cdot CO₂ adducts as carbone transfer agents provides a convenient alternative to the use of air- and moisture-sensitive carbene reagents, while ensuring high yields of organometallic products. The potential of this strategy was already underlined by Crabtree et al., who successfully isolated a variety of late transition metal-NHC complexes by reacting 1,3-dimethylimidazolium-2-carboxylate with suitable metal precursors, including the dichloro(p-cymene)ruthenium(II) dimer.¹²

Attempts to prepare the $[RuCl_2(p-cymene)(IMes)]$ complex (2) by refluxing $[RuCl_2(p-cymene)]_2$ with 2 equiv of

IMes \cdot CS₂ in THF or toluene failed. In all cases, ¹³C NMR analysis of the crude reaction mixtures revealed the persistence of signals in the 195-225 ppm region, thereby showing that elimination of CS₂ had not occurred, even after prolonged heating under a slow stream of argon. In view of the great stability displayed by NHC · CS₂ adducts in solution or in the solid state (cf. Figure 1), this observation is not surprising. Indeed, a survey of the literature confirmed that none of the various reactions of diaminocarbeniumdithiocarboxylate species reported thus far involved the regeneration of diaminocarbenes.²⁵ Unlike the CO₂ adducts, which readily dissociate and can be viewed as convenient surrogates for free NHCs, the CS₂ betaines retain their zwitterionic nature throughout chemical transformations. Thus, their reactivity is determined mainly by the presence of a Lewis acid center in the imidazol(in)ium ring, while the CS_2^- group acts as a Lewis or Brønsted base. To the best of our knowledge, this dual behavior has been exploited in two organocatalytic applications so far, namely, the cyanosilylation of aldehydes with trimethylsilyl cyanide²⁶ and the Staudinger reaction of ketenes with imines.²⁷

In light of the above considerations, we decided to apply the experimental procedure originally devised by Miguel et al. for the preparation of $[RuCl(arene)(PR_3 \cdot CS_2)]PF_6$ complexes (arene = benzene, *p*-cymene, or hexamethylbenzene, $PR_3 = PiPr_3$ or PCy_3) to the reaction of $[RuCl_2 (p-\text{cymene})]_2$ with NHC·CS₂ adducts.²⁸ Thus, the two partners were refluxed in ethanol for 3 h in the presence of excess carbon disulfide and potassium hexafluorophosphate under a slow stream of argon, followed by filtration and evaporation of the volatiles. Under these conditions, the dithiocarboxylate anions cleaved the μ -chloro bridges of the ruthenium dimer to afford new cationic complexes with the generic formula [RuCl(p-cymene)(NHC·CS₂)]PF₆ in high yields. Because TGA analyses had shown that $NHC \cdot CS_2$ betaines were far more stable than the phosphonium dithiocaboxylates employed by the Spanish team,¹⁹ we reasoned that they might as well react with the ruthenium dimer under less stringent conditions. To test this hypothesis, a streamlined protocol involving the use of stoichiometric amounts of $[RuCl_2(p-cymene)]_2$ (1 equiv), NHC · CS₂ adducts, and KPF₆ (2 equiv each) was devised. No carbon disulfide was added, and the whole transformation was carried out in ethanol at 60 °C under normal atmosphere (Scheme 4). Gratifyingly, the reactions proceeded very cleanly, and full conversions were atttained within 1 h.²⁹ The inorganic byproduct (KCl) was removed by filtration through Celite to afford almost quantitative yields of ruthenium-arene complexes bearing imidazol(in)ium-2-dithiocarboxylate ligands (4-8). These compounds were further purified by recrystallization from chloroform/cyclohexane. It should be noted that losses of materials occurred mainly during this final step, but we did not attempt to optimize it.

Products **4–8** were isolated as dark solids that did not show any sign of decomposition after more than two years of

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Scheme 4. Synthesis of Ruthenium-Arene Complexes Bearing Imidazol(in)ium-2-dithiocarboxylate Ligands



storage at room temperature under normal atmosphere. Their high stability was also evidenced by the fact that identical UV/visible spectra were recorded in acetonitrile, whether the solutions were freshly made or kept with no particular precautions in a closed vessel for more than two weeks. Analytical and spectroscopic data supported the structures depicted in Scheme 4. ¹H NMR analysis showed the presence of two doublets at ca. 5.5 and 5.7 ppm, respectively, assigned to the aromatic protons of the η^6 -(p-cymene) ligand, while ¹³C NMR spectra displayed a strongly deshielded signal at 212–218 ppm, due to the $CS_2^$ group coordinated as a $\kappa^2 S, S'$ chelate to the ruthenium center. The catalytic activity of cationic complexes 4-7 was probed in the ROMP of cyclooctene for 2 h at 60 °C, but, as expected, they did not afford any polymer. The metathetical activity of compound 8 was further screened in RCM and ROMP reactions using the standard characterization system proposed by Grubbs and co-workers.³⁰ Yet, for both the ring-closing metathesis of diethyl diallylmalonate and the ring-opening metathesis polymerization of cyclooctadiene, no sign of evolution was detected by NMR spectroscopy after 15 h in CD₂Cl₂ at 30 °C using 1 mol % of catalyst 8. We are currently investigating other rutheniumcatalyzed processes that might benefit from the use of stable cationic complexes such as compounds 4-8, and we shall report on them in due course.

Whereas phosphine–carbon disulfide adducts³¹ and other 1,1-dithiolate species,³² including dithiocarbamate, xanthate, and thioxanthate anions, have been widely employed as



Figure 2. Molecular conformation (ORTEP diagram) of [RuCl-(*p*-cymene)(IMes \cdot CS₂)]PF₆ (5) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and the PF₆⁻ counterion were omitted for the sake of clarity.

 $\kappa^1 S$, $\kappa^2 S$, S', or $\kappa^3 S$, C, S' ligands in mono- and binuclear metal complexes for several decades,³³ the coordination chemistry of NHC·CS₂ betaines is still a largely uncharted territory. Preliminary experiments in this field were conducted by Borer et al., who showed that 1,3-dimethylimidazolium-2-dithiocarboxylate formed stable complexes with a range of transition metal halides or nitrates.³⁴ The products obtained were characterized by IR and UV/visible spectroscopies only. Measurements of electrical conductivity, magnetic susceptibility, or cyclic voltammetry complemented the analyses in some cases, but no NMR or XRD analyses were reported. Thus, the accurate structure of the products obtained and the mode of binding of the zwitterionic ligand remained highly speculative. This prompted us to further investigate the structural features of complexes **4–8**.

X-ray Diffraction Analysis. Crystals of [RuCl(p-cymene)- $(IMes \cdot CS_2)$]PF₆ (5) suitable for X-ray diffraction analysis were grown from acetonitrile. Their molecular structure is depicted in Figure 2 and compared with those reported previously for the related ruthenium-arene complex $[RuCl_2(p-cymene)(IMes)] \cdot CHCl_3 (9)^{23}$ and the free IMes. CS_2 ligand (10)¹⁹ in Figure 3. This figure also shows the common atom-numbering system adopted to label the selected bond lengths and angles listed in Table 3. As expected, complex 5 displayed the distinctive three-legged piano stool geometry already observed in complex 9 and in many other ruthenium-arene species.³⁵ Chelation of ruthenium with the betaine adduct via its CS_2^- moiety led to a reduction of the S1-C6-S2 bite angle from 129.1(4)° to 112.3(2)° but did not significantly affect the C-S bond distances that remained close to 1.67 Å in both complexed and uncomplexed structures. Within each molecule, the C6-S1 and C6-S2 distances were very similar, indicating that the negative charge was equally spread over the two sulfur atoms. It should be pointed out that in the case of

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Figure 3. Atom-numbering system and molecular structures of $[RuCl(p-cymene)(IMes \cdot CS_2)]PF_6$ (5), $[RuCl_2(p-cymene)(IMes)] \cdot CHCl_3$ (9), and IMes $\cdot CS_2$ (10). Hydrogen atoms and cocrystallized counterions or solvent molecules were omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) Derived from Crystal Structures of [RuCl(*p*-cymene)(IMes · CS₂)]PF₆ (5), [RuCl₂(*p*-cymene)(IMes)] · CHCl₃ (9),^{*a*} and IMes · CS₂ (10)^{*b*}

compound	C6-S1	C6-S2	C2-C6	N1-C2	N3-C2	N1-C1a	C4-C5
5	1.680(3)	1.673(2)	1.464(3)	1.351(3) 1.370(3)	1.342(3)	1.460(3) 1.449(5)	1.324(4) 1.312(3)
10 ^c	1.667(3) 1.669(3)	1.667(3) 1.669(3)	1.483(8) 1.489(7)	1.370(3) 1.387(6) 1.374(6)	1.376(3) 1.387(6) 1.374(6)	1.449(5) 1.461(6) 1.456(6)	1.312(3) 1.318(11) 1.341(10)
compound	S1-C6-S2	N1-C2-N3		N1-C2-C6-S1	N1-C2-C6-S2		C1b-C1a-N1-C2
5 9	112.3(2)	107.3(1) 102.0(2)		48.1(2)	-136.2(2)		77.8(2) 87.2(3)
10 ^c	129.1(4) 129.1(4)	107.2(4) 106.4(5)		-65.3(2) -62.1(2)	118.0(5) 114.7(5)		104.9(6) 106.6(6)

^{*a*} Data from ref 23. ^{*b*} Data from ref 19. ^{*c*} Two molecules are present in the asymmetric unit.

IMes \cdot CS₂ (10) equivalence of both C–S distances resulted from C_2 symmetry in the crystal structure. Thus, only half of the molecule formed the asymmetric unit, while the other half was generated by symmetry. Moreover, the lengths of the two C–S bonds were much closer to the distances reported for common C=S double bonds (1.67 Å) than those of single C–S bonds (1.75 Å).³⁶

The imidazolium ring and the dithiocarboxylate unit were not coplanar (see torsion angles N1–C2–C6–S in Table 3). Nearly orthogonal conformations were observed in acyclic carbenium dithiocarboxylates³⁷ and in all but one of the other imidazol(in)ium-2-carboxylates^{9,11c,38} and their dithio^{19,39,40} or diseleno⁴⁰ analogues investigated so far by XRD analysis. The distortion was, however, less pronounced in complex **5** than in free IMes·CS₂. This could result from less favorable Coulombic interactions between the carbenium ion carbon and the lone pair of electrons on the sulfur atoms.⁴⁰ The C2–C6 exocyclic bond was also significantly shorter in [RuCl(*p*-cymene)(IMes·CS₂)]⁺ when compared to the free betaine. This indicates greater electron delocalization from the dithiocarboxylate unit to the imidazolium ring in the presence of the positively charged Ru cation, as further evidenced by shorter N1–C2 and N3–C2 bonds in the

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presence of the metal. Interestingly, the geometry of the heterocyclic ring suffered more distortions in complex **5** involving IMes·CS₂ than in complex **9**, containing the IMes carbene. Besides, the relative orientation of the *p*-cymene ligand was different in the two complexes (see Figure 3), but the distance between the centroid of the arene and the metal center remained almost the same in the crystal structures of [RuCl(*p*-cymene)(IMes·CS₂)]PF₆ (1.710 Å) and [RuCl₂-(*p*-cymene)(IMes)]·CHCl₃ (1.716 Å).

In all three structures under scrutiny, the N1–C2 and N3–C2 bond distances were (nearly) equal (Table 3) and indicated a significant C=N double-bond character, consistent with electronic conjugation within the N₂C⁺ motif. Electronic effects of the N-substituting aromatic rings were not transferred to the imidazolium ring motif. This was underlined by rather long N–C inter-ring distances, closer to a single N–C bond (1.47 Å) than to a double N=C bond (1.34 Å),³⁶ and by a perpendicular orientation of the mesityl groups versus the central heterocycle (cf. torsion angle C1b–C1a–N1–C2 in Table 3). Deviation from orthogonality was more pronounced in complex **5** (77.8(2)°) than in complex **9** (87.2(3)°) and in the free zwitterionic ligand **10** (ca. 106°), probably due to steric effects.

IR and UV/Visible Spectroscopies. The FT-IR spectra of complexes 4-8 were recorded in KBr pellets. In all cases, the two strongest signals were due to the P-F stretching and bending vibrations of the PF_6^- anion located at 842 and 558 cm⁻¹, respectively.⁴¹ Changes brought to the coordination sphere of ruthenium by varying the NHC \cdot CS₂ ligand had no influence on the position of these peaks. In addition to the various C-C and C-H stretching vibration bands, two remarkable absorptions originated from the organic subunits of the molecules, namely, the asymmetric stretching vibrations of the N_2C^+ and CS_2^- groups (Table 4). The former amidinium unit gave rise to a medium-intensity band located at ca. 1475 cm^{-1} for aromatic imidazolium cycles and at ca. 1555 cm^{-1} in complexes 7 and 8 sporting an imidazolinium ring. A second characteristic absorption of medium intensity was present in the 1010-1060 cm⁻¹ region and assigned to the asymmetric stretching of the dithiocarboxylate group. We failed to identify the corresponding symmetric stretching vibration bands in the experimental spectra of complexes 4-8. On the basis of theoretical calculations performed on 1,3-dimethylimidazolium-2-dithiocarboxylate, they are expected to be very weak and located below $900 \text{ cm}^{-1.40}$.

Comparison of the $\bar{\nu}_{asym}(N_2C^+)$ and $\bar{\nu}_{asym}(CS_2^-)$ wavenumbers recorded for $[RuCl(p-cymene)(NHC \cdot CS_2)]PF_6$ complexes 4-6 and the corresponding NHC·CS₂ free ligands showed that the imidazolium moiety of these zwitterions was not affected by complexation. Indeed, almost identical frequencies were obtained for the $N-C=N^+$ stretching vibrations in both complexed and uncomplexed betaines (Table 4). On the other hand, the absorption bands for the $S=C-S^{-}$ asymmetric stretching were significantly shifted to lower energy upon coordination, in good agreement with the formation of a chelate between the dithiocarboxylate unit of the ligand and the metal center. In the case of imidazolinium-based ligands SIMes \cdot CS₂ and SIDip \cdot CS₂, both the $\bar{\nu}_{asym}(N_2C^+)$ and $\bar{\nu}_{asym}(CS_2^-)$ stretching vibrations underwent changes upon coordination, although they were shifted in opposite directions.

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Table 4. Wavenumbers of IR Stretching Vibrations Bands (cm⁻¹) in [RuCl(*p*-cymene)(NHC·CS₂)]PF₆ Complexes (4–8) and the Corresponding NHC·CS₂ Free Ligands

complex	$\begin{array}{c} \bar{\nu}_{asym} \\ (N_2 C^+) \end{array}$	$\overline{\nu}_{asym}$ (CS ₂)	free ligand	$ar{ u}_{ m asym} \ ({ m N_2C^+})^a$	$\overline{\nu}_{asym}$ $(CS_2^-)^a$
4	1474	1029	$ICy \cdot CS_2$	1474	1058
5	1485	1025	$IMes \cdot CS_2$	1488	1052
6	1470	1010	$IDip \cdot CS_2$	1469	1058
7	1559	1032	SIMes · CS ₂	1531	1064
8	1549	1058	$SIDip \cdot CS_2$	1524	1080
^{<i>a</i>} Data f	from ref 19.		*		

Examination of the UV/visible spectra of [RuCl(*p*cymene)(NHC·CS₂)]PF₆ complexes 4–7 dissolved in acetonitrile revealed the presence of weak absorption bands in the visible domain (NHC = ICy: 489 and 580 nm, IMes: 518 nm, IDip: 550 nm, SIMes: 513 nm) due to $n \rightarrow \pi^*$ transitions within the dithiocarboxylate group, which are responsible for the dark colors of these compounds. Several other absorption maxima leading to well-shaped peaks or poorly defined shoulders were also detected in the UV part of the spectra. They are most likely caused by $\pi \rightarrow \pi^*$ transitions within the CS₂ group, the phenyl rings, and the aromatic imidazolium heterocycles,^{34,42} but we have not investigated in more detail their exact assignments.

Conclusion

The ability of imidazol(in)ium-2-carboxylates and dithiocarboxylates to act as NHC precursors for in situ catalytic applications was probed in ruthenium-promoted ring-opening metathesis and atom transfer radical polymerizations. Results obtained with the NHC·CO₂ adducts were in line with those reported previously starting from preformed [RuCl₂(*p*-cymene)(NHC)] complexes, whereas 1:2 mixtures of [RuCl₂(*p*-cymene)]₂ dimer and NHC·CS₂ zwitterions were almost completely inactive in the reactions under consideration. Comparison of TGA curves recorded for both types of adducts showed that NHC·CO₂ betaines were more labile than their CS₂ analogues and therefore more likely to release carbene ligands upon thermal activation.

To further rationalize the difference of catalytic activities observed, we have investigated thoroughly the preparation of preformed ruthenium-arene complexes from [RuCl2-(p-cymene)]₂ and NHC · CX₂ inner salts. In a first series of experiments, the ruthenium dimer was refluxed for 2 h in THF with 2 equiv of ICy \cdot CO₂, IMes \cdot CO₂, or IDip \cdot CO₂. As expected, the corresponding [RuCl₂(p-cymene)(NHC)] complexes (1-3) were isolated in high yields. From a practical point of view, this procedure is particularly attractive because it does not involve the manipulation of air- and moisture-sensitive free carbenes. When similar reactions were carried out with IMes · CS₂, ¹³C NMR spectroscopy revealed that the dithiocarboxylate unit was not cleaved off. Thus, in a second series of experiments, the reaction between $[RuCl_2(p-cymene)]_2$ and NHC \cdot CS₂ adducts was performed in the presence of potassium hexafluorophosphate for 1 h at 60 °C. Ethanol acted as solvent, and no particular precautions were taken to exclude air and moisture. Under these conditions, new cationic complexes (4-8) with the generic formula [RuCl(p-cymene)(NHC·CS₂)]PF₆ were isolated in

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high yields. These stable, 18-electron species are the first examples of well-defined transition-metal complexes bearing NHC·CS₂ ligands. They were characterized by various analytical techniques, and the molecular structure of compound **5** was determined by X-ray diffraction analysis. As expected from the in situ catalytic screening, they did not show any metathetical activity in ROMP or RCM reactions, but we are currently assessing their potentials in other ruthenium-catalyzed transformations.

Experimental Section

General Comments. Unless otherwise specified, all the syntheses were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were distilled from appropriate drying agents and deoxygenated prior to use. Imidazol(in)ium-2-carboxylates⁷ and dithiocarboxylates¹⁹ were synthesized according to published procedures. The [RuCl₂-(p-cymene)]₂ dimer⁴³ was purchased from Strem. Anhydrous neutral alumina W200 was obtained from Woelm, Eschwege (Germany). All the other chemicals were obtained from Aldrich. ¹H and ¹³C NMR spectra were recorded at 298 K with a Bruker DRX 400 spectrometer operating at 400.13 and 100.62 MHz, respectively. Chemical shifts are listed in parts per million downfield from TMS and are referenced from the solvent peaks or TMS. Infrared spectra were recorded with a Perkin-Elmer Spectrum One FT-IR spectrometer. UV/visible spectra were recorded with a Hewlett-Packard HP 8453 spectrophotometer. Thermogravimetric analyses were performed with a TA Q500 instrument using a 5 °C/min ramp. Gas chromatography was carried out with a Varian 3900 instrument equipped with a flame ionization detector and a WCOT fused silica column (stationary phase: CP-Sil 5CB, column length: 15 m, inside diameter: 0.25 mm, outside diameter: 0.39 mm, film thickness: 0.25 μ m). Size-exclusion chromatography (SEC) was performed in THF at 45 °C with a SFD S5200 autosampler liquid chromatograph equipped with a SFD 2000 refractive index detector and a battery of 4 PL gel columns fitted in series (particle size: 5 μ m; pore sizes: 10⁵, 10⁴, 10³, and 10² Å; flow rate: 1 mL/min). The molecular weights (not corrected) are reported versus monodisperse PMMA standards used to calibrate the instrument. Elemental analyses were carried out in the Laboratory of Pharmaceutical Chemistry at the University of Liège.

ROMP of Cyclooctene. A 25 mL round-bottom flask equipped with a magnetic stirring bar and capped with a three-way stopcock was charged with [RuCl₂(p-cymene)]₂ (9.2 mg, 0.015 mmol) and an imidazol(in)ium-2-(dithio)carboxylate (0.03 mmol). Air was expelled by applying three vacuum/ argon cycles before dry chlorobenzene (5 mL) and cyclooctene (1 mL, 7.5 mmol) were added with dried syringes under argon. The reaction mixture was stirred for 2 h in an oil bath at 60 °C. It was irradiated with a 40 W "cold white" fluorescent tube placed 10 cm away from the Pyrex reaction flask. The conversion was monitored by gas chromatography using the cyclooctane impurity of cyclooctene as internal standard. The resulting gel was diluted with chloroform (20 mL) and slowly poured into methanol (500 mL) under vigorous stirring. The precipitated polyoctenamer was filtered with suction, dried overnight under dynamic vacuum, and characterized by SEC and NMR.

ATRP of MMA. A 25 mL glass tube containing a magnetic stirring bar and capped with a three-way stopcock was charged with $[RuCl_2(p-cymene)]_2$ (3.6 mg, 0.006 mmol) and an imidazol-(in)ium-2-(dithio)carboxylate (0.012 mmol). Air was expelled by applying three vacuum/nitrogen cycles before methyl methacrylate (1 mL, 9.35 mmol) and ethyl 2-bromo-2-methylpropionate (0.1 M in toluene, 0.25 mL) were added with dried syringes

under nitrogen. The reaction mixture was heated for 16 h in an oil bath at 85 °C. After cooling to room temperature, it was diluted with THF (5 mL) and poured in *n*-heptane (600 mL) under vigorous stirring. The precipitated polymer was filtered with suction, dried overnight under dynamic vacuum, and characterized by SEC.

Preparation of Ruthenium-Arene Complexes Using Carboxylate Precursors. A 250 mL round-bottom flask equipped with a magnetic stirring bar and a reflux condenser topped with an oil bubbler was charged with [RuCl₂(*p*-cymene)]₂ (0.5 g, 0.82 mmol) and an imidazol(in)ium-2-carboxylate (1.71 mmol, 2.1 equiv). The reactor was purged of air by applying three vacuum/argon cycles before dry and degassed THF (100 mL) was added. The resulting suspension was refluxed for 2 h under a slow stream of argon, leading to the formation of a dark brown solution. The reaction mixture was brought back to room temperature, and the solvent was removed under reduced pressure to afford a dark brown residue, which was washed with *n*-pentane $(2 \times 20 \text{ mL})$. The remaining solid was dissolved in dichloromethane (10 mL). Neutral alumina (0.2 g) was added to the solution, and the solvent was removed under reduced pressure. The resulting freeflowing powder was dry-loaded on a short plug of neutral alumina (0.2 g). This column was eluted using a gradient of hexanes/dichloromethane from 1:0 to 0:1 v/v. The initial fractions containing p-cymene traces were discarded. In some cases, a small amount of methanol (2%) was added to dichloromethane in order to improve the recovery of product from the column. The resulting brown solution was washed with water to remove the last traces of imidazolium salt. It was evaporated on a rotary evaporator and dried under high vacuum.

RuCl₂(*p***-cymene)ICy (1):** brown solid (0.79 g, 89% yield); NMR data were in accord with literature values.²¹

RuCl₂(*p***-cymene)IMes (2):** brown solid (0.85 g, 85% yield); NMR data were in accord with literature values.^{22–24}

RuCl₂(*p***-cymene)IDip (3):** brown solid (0.81 g, 71% yield); NMR data were in accord with literature values.²²

Preparation of Ruthenium–Arene Complexes with Dithiocarboxylate Ligands. A 50 mL round-bottom flask equipped with a magnetic stirring bar was charged with $[\text{RuCl}_2(p\text{-cymene})]_2$ (0.1225 g, 0.2 mmol), an imidazol(in)ium-2-dithiocarboxylate (0.4 mmol), and potassium hexafluorophosphate (0.0736 g, 0.4 mmol). Reagent grade, denaturated ethanol (20 mL) taken straight from the bottle was added, and the reaction mixture was heated for 1 h under normal atmosphere in an oil bath at 60 °C. After cooling to room temperature, the volatiles were evaporated under vacuum. The residue was taken up with dichloromethane (10 mL) and filtered through a short plug of Celite. The inorganic salts were rinsed with dichloromethane (2×5 mL), and the filtrate was evaporated on a rotary evaporator. The crude product was recrystallized from chloroform/ cyclohexane and dried under high vacuum.

[RuCl(*p***-cymene)(ICy·CS₂)]PF**₆ (4): dark green, microcrystalline powder (0.23 g, 80% yield). ¹H NMR (400 MHz, CDCl₃): δ 1.22–1.45 (m, 6 H, Cy), 1.32 (d, ³*J*_{HH}=6.8 Hz, 6 H, *p*-cym CH-(C*H*₃)₂), 1.60–1.74 (m, 6 H, Cy), 1.86 (br d, 4 H, Cy), 2.04 (br d, 4 H, Cy), 2.37 (s, 3 H, *p*-cym CH₃), 2.87 (sept, ³*J*_{HH}=6.8 Hz, 1 H, *p*-cym C*H*(CH₃)₂), 4.52 (m, 2 H, CHN), 5.72 (d, ³*J*_{HH}=5.8 Hz, 2 H, *p*-cym CH_{ar}), 5.97 (d, ³*J*_{HH}=5.8 Hz, 2 H, *p*-cym CH_{ar}), 7.53 (s, 2 H, Im-C4,5) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 19.6, 22.9, 23.0, 25.0, 32.6, 33.6, 59.1, 85.7, 85.9, 105.5, 107.0, 120.0, 141.3, 218.1 (CS₂) ppm. IR (KBr): $\bar{\nu}$ 2933, 2859, 1564, 1474, 1452, 1202, 1029, 841, 710, 558 cm⁻¹. UV/vis (MeCN): λ (ε) 217 (25 200), 238 (22 900), 291 (9300), 371 (5000), 489 (2300), 580 (1400) nm (M⁻¹ cm⁻¹). Anal. Calcd for C₂₆H₃₈ClF₆N₂PRuS₂ (724.22): C, 43.12; H, 5.29; N, 3.87; S, 8.86. Found: C, 43.31; H, 5.35; N, 4.17; S, 8.16.

[RuCl(*p*-cymene)(IMes·CS₂)]PF₆ (5): dark purple, microcrystalline powder (0.24 g, 75% yield). ¹H NMR (400 MHz, CDCl₃): δ 1.07 (d, ³J_{HH} = 6.4 Hz, 6 H, *p*-cym CH(CH₃)₂), 2.04 (s, 12 H, *ortho*-CH₃), 2.14 (s, 3 H, *p*-cym CH₃), 2.38 (s, 6 H,

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para-CH₃), 2.53 (sept, 1 H, *p*-cym C*H*(CH₃)₂), 5.46 (d, ${}^{3}J_{HH} =$ 5.6 Hz, 2 H, *p*-cym CH_{ar}), 5.65 (d, ${}^{3}J_{HH} =$ 5.6 Hz, 2 H, *p*-cym CH_{ar}), 7.03 (s, 4 H, *meta*-CH), 7.57 (s, 2 H, =CHN) ppm. 13 C NMR (100 MHz, CDCl₃): δ 17.6, 19.3, 21.4, 22.6, 32.3, 86.4, 86.6, 106.7, 106.8, 126.3, 130.1, 130.4, 136.8, 142.3, 212.4 (CS₂) ppm. IR (KBr): $\bar{\nu}$ 3171, 3145, 2962, 2922, 1608, 1552, 1485, 1384, 1233, 1025, 842, 720, 558 cm⁻¹. UV/vis (MeCN): λ (ε) 197 (81900), 313 (10 700), 396 (4000), 518 (3300) nm (M⁻¹ cm⁻¹). Anal. Calcd for C₃₂H₃₈ClF₆N₂PRuS₂ (796.28): C, 48.27; H, 4.81; N, 3.52; S, 8.05. Found: C, 48.14; H, 4.59; N, 3.71; S, 8.24.

[RuCl(*p*-cymene)(IDip · CS₂)]PF₆ (6): dark blue, microcrystalline powder (0.24 g, 69% yield). ¹H NMR (400 MHz, CDCl₃): δ 1.06 (d, ³*J*_{HH} = 5.6 Hz, 6 H, *p*-cym CH(C*H*₃)₂), 1.19–1.24 (m, 24 H, IDip CH(C*H*₃)₂), 2.09 (s, 3 H, *p*-cym CH₃), 2.32 (sept, ³*J*_{HH} = 6.0 Hz, 4 H, IDip CH(CH₃)₂), 2.48 (sept, ³*J*_{HH} = 6.6 Hz, 1 H, *p*-cym CH(CH₃)₂), 5.41 (d, ³*J*_{HH} = 5.0 Hz, 2 H, *p*-cym CH_{ar}), 5.58 (d, ³*J*_{HH} = 5.0 Hz, 2 H, *p*-cym CH_{ar}), 7.36 (d, ³*J*_{HH} = 6.8 Hz, 4 H, *meta*-CH), 7.62 (t, ³*J*_{HH} = 7.2 Hz, 2 H, *para*-CH), 7.71 (s, 2 H, =CHN) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 19.5, 22.8, 23.1, 24.9, 29.6, 32.3, 81.1, 87.3, 106.4, 107.5, 125.6, 127.7, 130.1, 132.8, 136.8, 145.2, 211.8 (CS₂) ppm. IR (KBr): $\bar{\nu}$ 3175, 2966, 2930, 2872, 1549, 1471, 1389, 1368, 1207, 1061, 1010, 843, 804, 756, 722, 558 cm⁻¹. UV/vis (MeCN): λ (ε) 193 (88000), 238 (22800) shoulder, 328 (11600), 550 (4200) nm (M⁻¹ cm⁻¹). Anal. Calcd for C₃₈H₅₀ClF₆N₂PRuS₂ (880.45): C, 51.84; H, 5.72; N, 3.18; S, 7.28. Found: C, 51.09; H, 5.71; N, 3.42; S, 7.01.

[RuCl(*p*-cymene)(SIMes·CS₂)]PF₆ (7): dark purple, microcrystalline powder (0.22 g, 69% yield). ¹H NMR (400 MHz, CD₂Cl₂): δ 0.96 (d, ³*J*_{HH} = 6.8 Hz, 6 H, *p*-cym CH(CH₃)₂), 2.09 (s, 3 H, *p*-cym CH₃), 2.33 (s, 18 H, mesityl CH₃), 2.40 (m, 1 H, *p*-cym CH(CH₃)₂), 4.32 (s, 4 H, CH₂N), 5.44 (d, ³*J*_{HH} = 6.0 Hz, 2 H, *p*-cym CH_{ar}), 5.63 (d, ³*J*_{HH} = 6.0 Hz, 2 H, *p*-cym CH_{ar}), 5.63 (d, ³*J*_{HH} = 6.0 Hz, 2 H, *p*-cym CH_{ar}), 6.98 (s, 4 H, *meta*-CH) ppm. ¹³C NMR (100 MHz, CD₂Cl₂): δ 17.9, 19.1, 21.0, 22.4, 32.2, 51.0, 86.1, 86.8, 107.4, 107.6, 130.1, 130.3, 135.8, 141.3, 156.2, 213.1 (CS₂) ppm. IR (KBr): $\bar{\nu}$ 2963, 2922, 1610, 1559, 1511, 1466, 1382, 1355, 1291, 1213, 1088, 1032, 842, 741, 689, 575, 558 cm⁻¹. UV/vis (MeCN): λ (ε) 195 (85 700), 513 (2400) nm (M⁻¹ cm⁻¹). Anal. Calcd for C₃₂H₄₀ClF₆N₂PRuS₂ (798.30): C, 48.15; H, 5.05; N, 3.51; S, 8.03. Found: C, 48.08; H, 4.98; N, 3.69; S, 8.02.

[RuCl(p-cymene)(SIDip·CS₂)]PF₆ (8): dark brown, microcrystalline powder (0.31 g, 89% yield). ¹H NMR (400 MHz, CDCl₃): δ 1.03 (d, ${}^{3}J_{HH} = 6.8$ Hz, 6 H, *p*-cym CH(CH₃)₂), 1.30 (d, ${}^{3}J_{HH} = 6.4$ Hz, 12 H, SIDip CH(CH₃)₂), 1.34 (d, ${}^{3}J_{HH} = 6.4$ Hz, 12 H, SIDip CH(CH₃)₂), 2.04 (s, 3 H, *p*-cym CH₃), 2.43 (sept, ${}^{3}J_{HH} = 6.8$ Hz, 1 H, *p*-cym CH(CH₃)₂), 2.94 (sept, ${}^{3}J_{HH} = 6.4$ Hz, 4 H, SIDip CH(CH₃)₂), 4.42 (s, 4 H, CH₂N), 5.40 (d, ${}^{3}J_{HH} = 6.0$ Hz, 2 H, *p*-cym CH_{ar}), 5.57 (d, ${}^{3}J_{HH} = 6.0$ Hz, 2 H, *p*-cym CH_{ar}), 5.57 (d, ${}^{3}J_{HH} = 6.0$ Hz, 2 H, *p*-cym CH_{ar}), 5.57 (d, ${}^{3}J_{HH} = 6.0$ Hz, 2 H, *p*-cym CH_{ar}), 7.49 (t, ${}^{3}J_{HH} = 7.6$ Hz, 2 H, *para*-CH) ppm. 13 C NMR (100 MHz, CDCl₃): δ 19.6, 22.8, 23.8, 25.8, 29.6, 32.2, 54.1, 87.8, 87.9, 105.9, 109.2, 125.2, 125.6, 130.0, 131.8, 146.4, 153.4, 211.8 (CS₂) ppm. IR (KBr): $\bar{\nu}$ 3175, 2968, 2928, 2870, 1591, 1549, 1504, 1466, 1445, 1389, 1360, 1323, 1285, 1083, 1058, 844, 805, 758, 687, 558 cm⁻¹. Anal. Calcd for C₃₈H₅₂ClF₆N₂PRuS₂ (882.45): C, 51.72; H, 5.94; N, 3.17; S, 7.27. Found: C, 51.23; H, 5.94; N, 3.42; S, 7.05.

X-ray Crystal Structure Determination. Data were collected at room temperature on a Gemini diffractometer (Oxford Diffraction Ltd.) equipped with a Ruby CCD detector using an Enhance (Mo) X-ray source. Data collection program: CrysAlis CCD (Oxford Diffraction Ltd.), data reduction: CrysAlis RED (Oxford Diffraction Ltd.), structure solution: SHELXS, structure refinement (on F^2): SHELXL-97,⁴⁴ data analysis: PLATON.⁴⁵ A multiscan procedure was applied to correct for absorption effects. Hydrogen atom positions were calculated and refined isotropically using a riding model. Disorder of the PF₆⁻ ion was refined.

Crystal Data for [RuCl(*p***-cymene)(IMes**·**CS**₂)]**PF**₆ (5): dark purple crystals (from MeCN), triclinic, $P\overline{1}$, a = 8.126(1) Å, b = 14.560(1) Å, c = 16.441(1) Å, $\alpha = 77.9(1)^{\circ}$, $\beta = 80.5(1)^{\circ}$, $\gamma = 77.2$ (1) °, V = 1841.0(1) Å³, Z = 2, $\rho_{calc} = 1.436$ g cm⁻³, $F_{000} = 812$, λ (Mo K α) = 0.71073 Å, $\theta_{max} = 28.20^{\circ}$, 52973 total measured reflections, 8363 independent reflections ($R_{int} = 0.0288$), 5698 observed reflections ($I > 2\sigma(I)$), $\mu = 0.710$ mm⁻¹, 451 parameters, R_1 (all data) = 0.0554, R_1 (observed data) = 0.0340, S = GooF = 1.049, Δ /s.u. = 0.002, residual $\rho_{max} = 0.872$ e Å⁻³, $\rho_{min} = -0.349$ e Å⁻³.

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Supporting Information Available: CIF file with crystallographic data for complex **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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