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Cationic η^3-Allylic Complexes. 4. Cationic η^3-Allylic Complexes of Nickel from *S*-Allyl-1,1,3,3-tetramethylthiouronium Salts[1]

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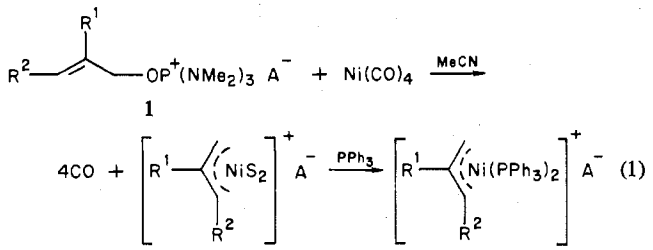
The oxidative addition of *S*-allyl-1,1,3,3-tetramethylthiouronium salts to zerovalent nickel complexes has been studied and gives rise to the formation of new cationic η^3-allylic complexes of nickel(II). The preparation of the starting salts is also described. Scope and limitations of the method are discussed.

Introduction

A number of recent studies have been concerned with the synthesis and reactions of cationic complexes of transition metals. Previous work has shown that the positive charge on the metal activates coordinated unsaturated ligands. Therefore homogeneous catalytic reactions of unsaturated C–C bonds have been found frequently to involve cationic allylic complexes.[2-7]

As a part of our continuing interest in the chemistry of cationic η^3-allylic complexes, we previously described the preparation of cationic η^3-allylic complexes of nickel from (allyloxy)tris(dimethylamino)phosphonium salt **1** (aTDP salts) and tetracarbonylnickel[8] (eq 1).



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R^1 = H, Me, Ph; R^2 = H, Me; A = ClO_4, PF_6, BF_4; S = hmpa, MeCN

As polysubstituted aTDP salts were not available,[9] this reaction could not be generalized. Thus, we decided to look for other starting materials with the same structural characteristics as aTDP salts, i.e.: the presence of a good leaving group, hexamethylphosphotriamide (hmpa), for aTDP salts and the presence of noncoordinating anions[10] such as PF_6^- or BF_4^-. It was found that *S*-allyl-1,1,3,3-tetramethylthiouronium salts (aTTU salts) had the required properties. In this paper we describe the preparation of these salts and the synthesis of the new η^3-allylbis(tetramethylthiourea)nickel salts from their reactions with zerovalent nickel complexes.

Results and Discussion

Synthesis and Characterization of *S*-Allyl-1,1,3,3-tetramethylthiouronium Salts. The reaction of thioureas and alkyl halides (eq 2) is a very old reaction[11,12] which gives *S*-alkyl

$$RX + S{=}C(NR^1R^2)_2 \rightarrow R{-}S{-}C(NR^1R^2)_2{}^+X^- \qquad X = Cl, Br, I \qquad (2)$$

pseudo thiouronium salts. It is well-known that this reaction occurs in the case of thiourea itself ($R^1 = R^2 = H$), but for allylic halides,[13] we failed to exchange easily the halide with any anions but picrate. The use of 1,1,3,3-tetramethylthiourea (TMTU) was more convenient; *S*-allyl-1,1,3,3-tetramethylthiouronium halides were simply prepared by mixing the allylic halide and TMTU in methanol. Addition of an aqueous solution of NH_4ClO_4, NH_4BF_4, KPF_6, or $NaBPh_4$ allowed the metathetical exchange of the halide and the isolation of *S*-allyl-1,1,3,3-tetramethylthiouronium salts **2–12** (reaction 3, Table I).

Table I

salt	X	allyl	A	yield,[a] %
2	Br	allyl	PF_6	89
3	Cl	methallyl	PF_6	96
4	Cl	methallyl	ClO_4	56
5	Cl	methallyl	BF_4	77
6	Cl	methallyl	BPh_4	62
7	Cl	crotyl	PF_6	100
8	Br	3,3-dimethylallyl	PF_6	89
9	Br	1,3-dimethylallyl	PF_6	56
10	Br	2-phenylallyl	PF_6	97
11	Br	cinnamyl	PF_6	100
12	Br	cyclohexenyl	PF_6	88

[a] Yields based on TMTU used.

$$\text{allyl–X} + S{=}C(NMe_2)_2 \xrightarrow[(2)\ A^-,H_2O]{(1)\ MeOH} [\text{allyl–S–C–}(NMe_2)_2]^+A^- \qquad (3)$$

2–12

The products were white crystalline solids (except **9** and **11**, obtained as colorless oils), which were characterized by elemental and spectroscopic analysis. ^1H NMR spectra (CD_3CN) show a singlet (δ ca. 3.2) for the protons of the NMe_2 groups which corresponds to a deshielding of δ 0.2 relative to the same protons in TMTU. ^{13}C spectra (broad-band decoupling, CH_3CN) give, besides the signals of the allyl moiety,

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Table II

starting salt	η^3-allyl	A	product	yield, %
2	allyl	PF_6	13	100
3	methallyl	PF_6	14	100
4	methallyl	ClO_4	15	100
5	methallyl	BF_4	16	94
6	methallyl	BPh_4	17	89
7	crotyl	PF_6	18	94
8	1,1-dimethylallyl	PF_6	19	86
9	1,3-dimethylallyl	PF_6	20	*a*
10	2-phenylallyl	PF_6	21	100
11	cinnamyl	PF_6	22	100
12	cyclohexenyl	PF_6	23	76

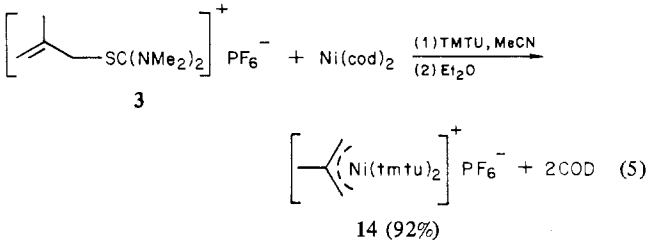
[a] Not isolated in a pure state.

two singlets at δ 42.7 and 174.2, respectively, attributed to the carbons of the NMe_2 and S–C–N_2[14] groups. These chemical shifts correspond to a deshielding of δ 1.1 and to a shielding of δ 20 relative to the same carbons in TMTU. All the NMR data agree well with the thiouronium structure. Infrared analyses confirm this result, and we can see a hypsochromic shift (ca. 100 cm^{-1}) of the ν(C–N) in S–C–N (1600–1610 cm^{-1} for the aTTU salts and 1510 cm^{-1} for TMTU[15]) corresponding to a shortening of the carbon–nitrogen bonds.

Synthesis and Characterization of (η^3-Allyl)bis(tetramethylthiourea)nickel Salts. Synthesis of (η^3-allyl)bis(tetramethylthiourea)nickel salts following the same procedure as previously reported for aTDP salts[8] failed. Nickel tetracarbonyl and aTTU salts did not react rapidly in acetonitrile, and a reaction was observed only (CO evolvement and coloration) when 1 equiv of TMTU was added. Moreover the evolved carbon monoxide must be flushed out of the reactor under a stream of argon in order to allow the reaction to go to completion. Under these conditions we were able to isolate crystalline compounds which according to chemical and spectroscopic analyses have the formula [(η^3-allyl)Ni(tmtu)$_2$]$^+$A$^-$ (reaction 4, Table II).

$$\underset{\textbf{2–12}}{[\text{allyl–S–C(NMe}_2)_2]^+A^-} + Ni(CO)_4 \xrightarrow[(2)\ Et_2O]{(1)\ TMTU,MeCN} \underset{\textbf{13–23}}{[(\eta^3\text{-allyl})Ni(tmtu)_2]^+A^-} \quad (4)$$

The use of $Ni(CO)_4$, which is extremely toxic,[16] could be avoided by using bis(1,5-cyclooctadiene)nickel, $Ni(cod)_2$ (eq 5). All complexes gave satisfactory elemental results. In-



(5)

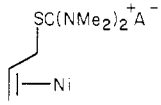
frared spectra contain the characteristic absorptions of PF_6 (560 and 840 cm^{-1}) and ClO_4 (420 and 620 cm^{-1}) anions and a strong absorption at 1560 cm^{-1} attributed to the CN stretching of the S–C–N bond in the coordinated TMTU (ν(CN) = 1510 cm^{-1} in the free ligand[15])—^{1}H NMR spectra are typical of the η^3-allyl structure.[17] The spectra of symmetric complexes **14–17** and **21** show singlets for syn and anti protons. For the nonsymmetric ones **18** and **22**, the spectra clearly indicate a syn configuration of the allyl ligand by a coupling constant ^3J(H–H) of 13 Hz between meso hydrogen and hydrogen on C_1. The same configuration is observed for the 1,3-dimethylallyl ligand although complex **20** could not be isolated. Only one doublet (δ 0.93, ^3J(H–H) = 6 Hz) for the two methyl groups and a triplet (δ 5.2, ^3J(H–H) = 12.5 Hz) for the meso hydrogen demonstrate a syn–syn stereochemistry of the ligand. All complexes give for TMTU protons only one singlet at δ 3.1. Most of the complexes were air stable in the solid state. They were soluble in dipolar aprotonic solvents but insoluble in water and other solvents. They did not react with water, but their solutions were rapidly decomposed in air. The formation of complexes was rapid and complete starting from primary aTTU salts but much slower from secondary ones. For salt **12** ca. 25% of the starting salt remained after 24 h. The reaction was still slower for salt **9**, and complex **20** decomposed during the reaction.

Mechanism. The reaction of aTTU salts and nickel tetracarbonyl gives rise to the formation of a nickel–carbon bond, formally resulting from an oxidative addition of an aTTU salt to a nickel(0) compound. Some mechanistic studies have been reported for the oxidative addition of an A–B molecule to a metal m in a low oxidation state:[18]

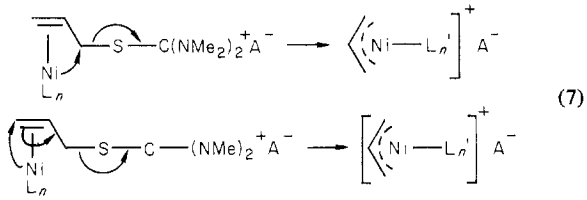
$$m + A\text{–}B \rightarrow A\text{–}m\text{–}B \quad (6)$$

Four mechanisms were proposed:[18a] S_N2[19a] or S_N2' type reactions, a three-center concerted reaction,[19b] a radical pathway,[19c] and a template reaction.[19c]

When the A–B molecule is an allylic halide, no unambiguous mechanism has been established. However a template reaction has been generally accepted: rapid and reversible formation of a metal–olefin complex followed by an S_N2' intramolecular rearrangement affords a η^3- or η^1-allylic complex.[19d] The nature of the intermediates in our reaction is not clear, but we assume that they are the same in all cases, probably of the type "NiL_n" with L = CO or tmtu. A radical pathway can be excluded since primary aTTU salts are more reactive than secondary ones. It seems reasonable to think that the first step, as for allylic halides, is the formation of a nickel–olefin complex



which reacts further by an intramolecular S_N2 or S_N2' process (eq 7).



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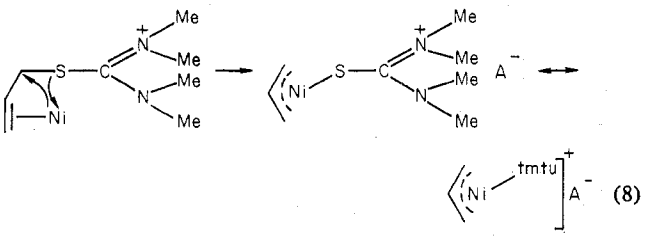
The lower rate of reaction observed for secondary aTTU salts compared to those of primary ones seems to be related to steric effects. For the case of the cyclohexenyl ligand (salt **12**), the formation of a η^3-allylic complex is unfavorable as the complex **22** has an extremely hindered anti–anti configuration. These facts, as well as very different reactivities of salts **8** compared to those of **9**, show that an S_N2' process is very unlikely. An S_N2-type mechanism agrees well with experimental results; however, we cannot exclude a three-center mechanism (eq 8).

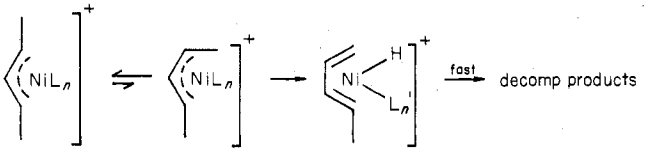


(8)

Stability of Complexes. The isolated complexes are stable if the starting aTTU salts are primary but decompose in solution when the ligand is the cyclohexenyl **23** or 1,3-dimethylallyl **20**.

In the case of complex **23** the anti–anti configuration of the cyclohexenyl ligand is favored over a β-hydride elimination often invoked to explain the kinetic instability of anti η^3-allylic complexes. The instability of complex **20** for which the 1,3-dimethylallyl ligand has a syn–syn configuration is rather surprising and is at variance with the order of stability proposed by Maitlis[20] for $(C_5Me_5)(\eta^3\text{-allyl})mCl$ (m = Rh, Ir) complexes. For this series, the complexes having this ligand are the most stable.

It is possible that in solution complex **20** is in equilibrium with an undetectable syn–anti species which undergoes a β-hydride elimination (eq 9).



(9)

Work is in progress to get insight into the mechanism of formation of these complexes, to explain the observed order of stability, and to explore the scope of catalytic activity in diene reactions. We shall also examine the reactivity of the complexes toward electrophiles and nucleophiles, and we think that such complexes will have some synthetic applications in organic synthesis.

Conclusion

The method reported here and the first described[8] are excellent and efficient routes for the rapid preparation of a wide variety of cationic $(\eta^3\text{-allyl})$nickel complexes and are the better ones as we have shown in a comparative study published elsewhere.[1]

Moreover they avoid the use of expensive silver and thallium salts, whose reactions and roles are not always clear in the synthesis and especially in the catalytic reactions of cationic complexes starting from neutral metal halides. We believe that these methods will be applied to other metals, and preliminary results have shown that they are effective at least for palladium complexes.[21]

Experimental Section

General Data. All operations for the preparation of complexes were performed under an argon (Air Liquide) atmosphere. Nickel tetracarbonyl is very flammable and toxic and must be handled in a well-ventilated hood. Nickel tetracarbonyl (Fluka) was filtered just before use. It must be replaced in all cases by bis(1,5-cyclooctadiene)nickel which is easily prepared.[22] Solvents were dried and deoxygenated by standard methods and stored under argon over molecular sieves. Elemental analyses were undertaken by the microanalytical central service of CNRS, Lyon, France.

Physical Measurements. IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer with use of KBr pellets or windows. ^1H and ^{13}C NMR spectra were taken on a Bruker HX90 or Perkin-Elmer R12B spectrometer. Chemical shifts are given in δ units downfield from tetramethylsilane as internal standard.

Materials. 1,3-Dimethylallyl bromide and 3,3-dimethylallyl bromide were prepared according to literature methods[23] by reacting concentrated HBr respectively with 3-penten-2-ol and dimethylvinylcarbinol. 3-Bromocyclohexene and 2-phenylallyl bromide were obtained by the *N*-bromosuccinimide method starting from cyclohexene[24] and α-methylstyrene.[25] Other starting chemicals were commercially available.

Synthesis of aTTU Salts 2–12. Equivalent amounts of TMTU and the allylic halide were dissolved in MeOH (1 M) and submitted to the indicated conditions. The reaction mixture was introduced into a separatory funnel containing an aqueous solution of 1.2 equiv of salt (NH_4ClO_4, KPF_6, $NaBPh_4$, NH_4BF_4) in 6 volumes of water. The aTTU salt generally precipitated or was decanted. The resulting two-phase system was washed with Et_2O and the aTTU salt extracted with CH_2Cl_2. Drying over $MgSO_4$ and evaporation of CH_2Cl_2 under reduced pressure generally left a white solid which could be recrystallized in an appropriate solvent.

***S*-Allyl-1,1,3,3-tetramethylthiouronium Hexafluorophosphate (2).** A 6.5-g sample of allyl bromide was used (room temperature, 44 h), yielding 14.2 g (89%) of **2**: mp 63–65 °C; ^1H NMR (CD_3CN) δ 3.2 (s, 12 H, NCH_3), 3.6 (d, 2 H, J(H–H) = 6.4 Hz, CH_2S), 5.05–5.25 (m, 3 H, CH_2=CH). Anal. Calcd for $C_8H_{17}F_6N_2PS$: C, 30.19; H, 5.38; N, 8.80. Found: C, 30.0; H, 5.6; N, 8.9.

***S*-Methallyl-1,1,3,3-tetramethylthiouronium Hexafluorophosphate (3).** A 4.53-g sample of methallyl chloride was used (60 °C, 18 h), yielding 15.9 g (96%) of **3**: mp 67 °C (AcOEt); ^1H NMR (CD_3CN) δ 1.85 (d, 3 H, J(H–H) = 1 Hz, CH_3), 3.21 (s, 12 H, NCH_3), 3.62 (s, 2 H, CH_2S), 4.95–5.05 (br, 2 H, CH_2=); ^{13}C NMR (CH_3CN) δ 19.3 (CH_3), 40.3 (CH_2S), 42.7 (NCH_3), 115.4 (H_2C=), 139.1 (=C–), 174.2 (SCN). Anal. Calcd for $C_9H_{19}F_6N_2PS$: C, 32.53; H, 5.76; N, 8.43. Found: C, 32.6; H, 5.6; N, 8.9.

***S*-Methallyl-1,1,3,3-tetramethylthiouronium Perchlorate (4).** A 1.91-g sample of methallyl chloride was used (room temperature, 73 h), yielding 3.2 g (56%) of **4**: mp 76 °C; ^1H NMR identical with that of salt **3**. Anal. Calcd for $C_9H_{19}ClN_2O_4S$: C, 37.69; H, 6.68; N, 9.77; Cl, 12.36. Found: C, 37.6; H, 6.3; N, 9.7; Cl, 13.6.

***S*-Methallyl-1,1,3,3-tetramethylthiouronium Tetrafluoroborate (5).** A 1.91-g sample of methallyl chloride was used (68 °C, 15 h), yielding 4.2 g (77%) of **5**: mp 69 °C; ^1H NMR identical with those of salts **3** and **4**. Anal. Calcd for $C_9H_{19}BF_4N_2S$: C, 39.43; H, 6.99; N, 10.22. Found: C, 39.4; H, 6.9; N, 10.3.

***S*-Methallyl-1,1,3,3-tetramethylthiouronium Tetraphenylborate (6).** A 1.91-g sample of methallyl chloride was used (room temperature, 88 h), yielding 6.3 g (62%) of **6**: mp 202 °C; ^1H NMR (CD_3CN) δ 1.8 (s, 3 H, CH_3), 3.08 (s, 12 H, NCH_3), 3.52 (s, 2 H, CH_2S), 4.94 (br, 2 H, CH_2=), 6.75–7.45 (br, 20 H, aromatic protons). Anal. Calcd for $C_{33}H_{39}BN_2S$: C, 78.25; H, 7.76; N, 5.53. Found: C, 78.4; H, 7.4; N, 5.3.

***S*-Crotyl-1,1,3,3-tetramethylthiouronium Hexafluorophosphate (7).** A 2.26-g sample of crotyl chloride was used (room temperature, 48 h), yielding 8.1 g (100%) of **7**: mp 76 °C (AcOEt); IR 1670 ($\nu_{C=C}$), 970 cm^{-1} (δ_{C-H}(trans)); ^1H NMR (CD_3CN) δ 1.67 (d, 3 H, J(H–H) = 5.3 Hz, CH_3), 3.16 (s, 12 H, NCH_3), 3.55 (d, 2 H, J(H–H) = 6 Hz, CH_2S), 5.1–6.1 (m, 2 H, HC=CH). Anal. Calcd for $C_9H_{19}F_6N_2PS$: C, 32.53; H, 5.76; N, 8.43. Found: C, 32.6; H, 5.6; N, 8.7.

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***S*-(3,3-Dimethylallyl)-1,1,3,3-tetramethylthiouronium Hexafluorophosphate (8).** A 7.45-g sample of 3,3-dimethylallyl bromide was used (room temperature, 3 h), yielding 15.5 g (89%) of **8**: mp 80 °C; ^{1}H NMR (CD_3CN) δ 1.72 (s, 6 H, CH_3), 3.19 (s, 12 H, NCH_3), 3.62 (d, 2 H, J(H–H) = 7.3 Hz, CH_2S), 5.28 (t, 1 H, –CH). Anal. Calcd for $C_{10}H_{21}F_6N_2PS$: C, 34.68; H, 6.11; N, 8.09. Found: C, 34.5; H, 6.2; N, 8.5.

***S*-(1,3-Dimethylallyl)-1,1,3,3-tetramethylthiouronium Hexafluorophosphate (9).** A 2.76-g sample of 1-3-dimethylallyl bromide was used (room temperature, 24 h), yielding 3.6 g (56%) of **9**: oil; IR 1670 ($\nu_{C=C}$), 980 cm^{-1} (δ_{C-H}(trans)); ^{1}H NMR (CD_3CN) δ 1.38 (d, 3 H, J(H–H) = 6.6 Hz, CH_3), 1.66 (d, 3 H, J(H–H) = 5 Hz, CH_3C=), 3.20 (s, 12 H, NCH_3), 3.8–4.4 (m, 1 H, –CHS), 5.0–6.0 (m, 2 H, HC=CH). Anal. Calcd for $C_{10}H_{21}F_6N_2PS$: C, 34.68; H, 6.11; N, 8.09. Found: C, 33.4; H, 6.2; N, 8.0.

***S*-(2-Phenylallyl)-1,1,3,3-tetramethylthiouronium Hexafluorophosphate (10).** A 4.73-g sample of 2-phenylallyl bromide was used (68 °C, 15 h), yielding 9.2 g (97%) of **10**: mp 72 °C; ^{1}H NMR (CD_3CN) δ 3.08 (s, 12 H, NCH_3), 4.2 (s, 2 H, CH_2S), 5.5–5.6 (s, H_2C=), 7.5 (s, aromatic protons). Anal. Calcd for $C_{14}H_{21}F_6N_2PS$: C, 42.64; H, 5.37; N, 7.10. Found: C, 42.3; H, 5.2; N, 7.8.

***S*-Cinnamyl-1,1,3,3-tetramethylthiouronium Hexafluorophosphate (11).** A 3.94-g sample of cinnamyl bromide was used (room temperature, 24 h), yielding 7.9 g (100%) of **11**: oil; IR 975 cm^{-1} (δ_{C-H}(trans)); ^{1}H NMR (CD_3CN) δ 3.2 (s, 12 H, NCH_3), 3.8 (d, 2 H, J(H–H) = 7.3 Hz, CH_2S), 6–6.85 (m, 2 H, HC=CH), 7.36 (s, 5 H, aromatic protons). Anal. Calcd for $C_{14}H_{21}F_6N_2PS$: C, 42.64; H, 5.37; N, 7.10. Found: C, 42.6; H, 5.5; N, 7.0.

***S*-(2-Cyclohexenyl)-1,1,3,3-tetramethylthiouronium Hexafluorophosphate (12).** A 8.1-g sample of 3-bromocyclohexene was used (room temperature, 48 h), yielding 15.9 g (88%) of **12**: mp 54 °C; ^{1}H NMR (CD_3CN) δ 1.55–2.2 (br, 6 H, CH_2 cycle), 3.23 (s, 12 H, NCH_3), 3.85–4.22 (br, 1 H, CHS), 5.45–6.20 (br, 2 H, HC=CH). Anal. Calcd for $C_{11}H_{21}F_6N_2PS$: C, 36.87; H, 5.91; N, 7.82. Found: C, 36.2; H, 5.7; N, 7.9.

Synthesis of (η^3-Allyl)bis(tetramethylthiourea)nickel Salts. A 5-mmol sample of the aTTU salt and a slight excess (5.1 mmol, 0.674 g) of TMTU were introduced in solid form into a 250-cm^3 reactor equipped with a condenser cooled to –25 °C by a stream of cold EtOH. The reactor was flushed with argon (30–50 cm^3 min^{-1}), and 5 cm^3 of CH_3CN was introduced. The reaction mixture was stirred until reactants dissolved, and an excess of nickel tetracarbonyl (10–20 mmol) was added in one batch by means of a syringe. An immediate red coloration developed and CO was evolved. The mixture was stirred until metallic nickel precipitated[26] and for a further 2 h to complete the reaction and the decomposition of $Ni(CO)_4$. After this time, about 0.5 cm^3 of solution was vented in a cold trap at –196 °C in order to eliminate excess $Ni(CO)_4$ eventually present. That could be controlled by adding a solution of I_2 in MeOH in the trap. Usually no $Ni(CO)_4$ was found. The red solution was then filtered and poured into 300 cm^3 of Et_2O. Orange to violet solids were precipitated and stirred with Et_2O during several hours before isolation.

The elemental analysis did not always fit very well with the calculated values due to the presence of traces of metallic nickel, which remained even after repeated purifications, and of solvation molecules, which could not be removed under prolonged vacuum drying. Unfortunately, the remaining solvent did not correspond to a stoichiometric ratio, but spectroscopic data demonstrated unambiguously the proposed structures.

(η^3-Allyl)bis(tetramethylthiourea)nickel Hexafluorophosphate (13). A 1.6-g sample of salt **2** was used, yielding 2.6 g (100%) of **13**. Anal. Calcd for $C_{13}H_{29}F_6N_4NiPS_2$: C, 30.66; H, 5.74; N, 11.00; Ni, 11.53. Found: C, 30.0; H, 5.7; N, 10.1; Ni, 13.1.

(η^3-Methallyl)bis(tetramethylthiourea)nickel Hexafluorophosphate (14). A 1.66-g, sample of salt **3** was used, yielding 2.6 g (100%) of **14**: orange solid; ^{1}H NMR (CD_3CN) δ 2.13 (s, 3 H, CH_3), 2.22 (s, 2 H, anti protons), 2.95 (s, 2 H, syn protons), 3.13 (s, 24 H, NCH_3). Anal. Calcd for $C_{14}H_{31}F_6N_4NiPS_2$: C, 32.14; H, 5.97; N, 10.71; Ni, 11.22. Found: C, 31.8; H, 6.1; N, 10.8; Ni, 13.0.

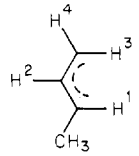
This complex could also be obtained by starting from $Ni(cod)_2$. The same experimental technique was used. One equivalent of solid $Ni(cod)_2$ was slowly added for 1 h. After 0.25 h of agitation, the homogeneous red solution obtained was filtered and 300 cm^3 of Et_2O was introduced, yielding 2.4 g (92%) of **14**.

(η^3-Methallyl)bis(tetramethylthiourea)nickel Perchlorate (15). A 1.43-g sample of salt **4** was used, yielding 2.4 g (100%) of **15**: orange solid; ^{1}H NMR (CD_3CN) identical with that of **14**. Anal. Calcd for $C_{14}H_{31}ClN_4NiO_4S_2$: C, 35.20; H, 6.54; N, 10.73; Cl, 7.42; Ni, 12.29. Found: C, 35.2; H, 6.5; N, 10.9; Cl, 7.6; Ni, 14.0.

(η^3-Methallyl)bis(tetramethylthiourea)nickel Tetrafluoroborate (16). A 1.37-g sample of salt **5** was used, yielding 2.2 g (94%) of **16**: orange solid; ^{1}H NMR (CD_3CN) identical with those of **14** and **15**. Anal. Calcd for $C_{14}H_{31}BF_4NiS_2$: C, 36.16; H, 6.72; N, 12.05; Ni, 12.62. Found: C, 35.8; H, 6.5; N, 12.4; Ni, 12.7.

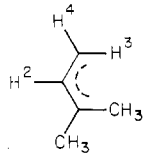
(η^3-Methallyl)bis(tetramethylthiourea)nickel Tetraphenylborate (17). A 2.53-g sample of salt **6** was used, yielding 3.1 g (89%) of **17**: orange solid; ^{1}H NMR (CD_3CN) δ 2.09 (s, 3 H, CH_3), 2.18 (s, 2 H, anti protons), 2.93 (s, 2 H, syn protons), 3.06 (s, 24 H, NCH_3), 6.6–7.5 (br, aromatic protons). Anal. Calcd for $C_{38}H_{51}BN_4NiS_2$: C, 65.44; H, 7.37; N, 8.03; Ni, 8.42. Found: C, 65.7; H, 7.4; N, 8.0; Ni, 9.1.

***(syn*-η^3-Crotyl)bis(tetramethylthiourea)nickel Hexafluorophosphate (18).** A 1.66-g sample of salt **7** was used, yielding 2.45 g (94%) of **18**: violet solid; ^{1}H NMR (CD_2Cl_2) δ 1.05 (d, 3 H, J(H–H^1) = 6 Hz, CH_3), 1.86 (dd, 1 H, J(H–H^2) = 12.7 Hz, J(H–H^4) = 1 Hz, H^3), 3.18 (s, 24 H, NCH_3), 5.11 (dt, 1 H, J(H–H^1) = J(H–H^3) = 12.7 Hz, J(H–H^4) = 6.7 Hz, H^2), H^1 and H^4 not attributed.



Anal. Calcd for $C_{14}H_{31}F_6N_4NiPS_2$: C, 32.14; H, 5.97; N, 10.71; Ni, 11.22. Found: C, 31.4; H, 5.9; N, 10.4; Ni, 11.6.

(η^3-1,1-Dimethylallyl)bis(tetramethylthiourea)nickel Hexafluorophosphate (19). A 1.75-g sample of salt **8** was used, yielding 2.3 g (86%) of **19**: orange solid; ^{1}H NMR (CD_3CN) δ 1.03 (s, 3 H, anti CH_3), 1.12 (s, 3 H, syn CH_3), 2.21 (dd, 1 H, J(H–H^2) = 12.7 Hz, J(H–H^4) = 2 Hz, H^3), 2.87 (dd, 1 H, J(H–H^2) = 8 Hz, J(H–H^3) = 2 Hz, H^4), 3.1 (s, 24 H, NCH_3), 5.15 (dd, 1 H, H^2).



Anal. Calcd for $C_{15}H_{33}F_6N_4NiPS_2$: C, 33.55; H, 6.19; N, 10.43; Ni, 10.93. Found: C, 32.3; H, 6.1; N, 10.5; Ni, 11.9.

Complex 20. A 1.73-g sample of salt **9** was used, but complex **20** could not be isolated in a pure state.

(η^3-2-Phenylallyl)bis(tetramethylthiourea)nickel Hexafluorophosphate (21). A 1.97-g sample of salt **10** was used, yielding 3 g (100%) of **21**: pink solid; ^{1}H NMR (CD_3CN) δ 2.42 (s, 2 H, anti protons), 3.07 (s, 24 H, NCH_3), 3.41 (s, 2 H, syn protons), 7.3–7.7 (br, 5 H, aromatic protons). Anal. Calcd for $C_{19}H_{33}F_6N_4NiPS_2$: C, 38.99; H, 5.68; N, 9.57; Ni, 10.03. Found: C, 37.4; H, 5.5; N, 9.7; Ni, 10.5.

***(syn*-η^3-Cinnamyl)bis(tetramethylthiourea)nickel Hexafluorophosphate (22).** A 1.97-g sample of salt **11** was used, yielding 3 g (100%) of **22**: ^{1}H NMR ($CDCl_3$) δ 2.28 (d, 1 H, J(H–H^2) = 13.3 Hz, H^3), 3.14 (s, 24 H, NCH_3), 3.73 (d, 1 H, J(H–H^2) = 12.7 Hz, H^1), 5.82 (dt, 1 H, J(H–H^1) = J(H–H^3) = 13 Hz, J(H–H^4) = 7.5 Hz, H^2), 7.33 (br, 5 H, aromatic protons), H^4 not attributed. Anal. Calcd for $C_{19}H_{39}F_6N_4NiPS_2$: C, 38.99; H, 5.68; N, 9.57; Ni, 10.03. Found: C, 38.6; H, 5.7; N, 7.2; Ni, 10.0.

(η^3-Cyclohexenyl)bis(tetramethylthiourea)nickel Hexafluorophosphate (23). A 1.79-g sample of salt **12** was used. After 24 h we obtained a mixture containing 76% of **23**, which was separated from the starting salt by washing with AcOEt: brown solid; ^{1}H NMR (CD_3CN) δ 1.3–1.7 (br, 6 H, CH_2 cycle), 3.1 (s, 24 H, NCH_3), 4–4.4 (br, 2 H, syn protons), 5.6 (t, 1 H, J(H–H) = 6.7 Hz, meso proton). Anal. Calcd for $C_{16}H_{33}F_6N_4NiPS_2$: C, 34.99; H, 6.06; N, 10.20; Ni, 10.69. Found: C, 32.9; H, 6.0; N, 9.9; Ni, 12.4.

(26) $Ni(CO)_4$ was used in a ca. fourfold excess as the reaction was carried out under a stream of argon. The end of reaction could be visualized by the precipitation of metallic nickel arising from the decomposition of $Ni(CO)_4$.

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Registry No. **2**, 75066-33-0; **3**, 75066-35-2; **4**, 75066-36-3; **5**, 75066-37-4; **6**, 75066-38-5; **7**, 75066-40-9; **8**, 75066-42-1; **9**, 75067-20-8; **10**, 75066-44-3; **11**, 75066-46-5; **12**, 75066-48-7; **13**, 75067-22-0; **14**, 65296-86-8; **15**, 75067-23-1; **16**, 75067-24-2; **17**, 75067-25-3; **18**, 75067-27-5; **19**, 75067-29-7; **21**, 75067-31-1; **22**, 75067-33-3; **23**, 75067-35-5; $S{=}C(NMe_2)_2$, 2782-91-4; $Ni(CO)_4$, 13463-39-3; allyl bromide, 106-95-6; methallyl chloride, 563-47-3; crotyl chloride, 591-97-9; 3,3-dimethylallyl bromide, 870-63-3; 2-phenylallyl bromide, 3360-54-1; cinnamyl bromide, 4392-24-9; cyclohexenyl bromide, 1521-51-3; $Ni(cod)_2$, 1295-35-8.

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Preparation and Derivatives of *cis*-$M(CO)_4(SiCl_3)_2$ (M = Fe, Ru, Os)

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The preparation of *cis*-$Ru(CO)_4(SiCl_3)_2$ by the ultraviolet irradiation of $Ru_3(CO)_{12}$ and excess Cl_3SiH in hexane under carbon monoxide is described. The method is readily extended to the iron and previously unknown osmium analogues. Whereas *cis*-$Ru(CO)_4(SiCl_3)_2$ readily undergoes substitution at room temperature with ligands (L) to give *mer*-$Ru(CO)_3L(SiCl_3)_2$, the iron and osmium compounds require much more forcing conditions. Further substitution in the ruthenium derivatives to yield $Ru(CO)_2L_2(SiCl_3)_2$ could only be achieved when L had a small cone angle. However, it was verified that the remaining equatorial carbonyl ligand in $Ru(CO)_3(PPh_3)(SiCl_3)_2$ was still labile with the facile synthesis of $Ru(CO)_2(PPh_3)[P(OCH_3)_3](SiCl_3)_2$. The ^{31}P NMR spectra of the phosphorus derivatives and the isomerization (at 120 °C) of *cis*-$Os(CO)_4(SiCl_3)_2$ are also discussed.

Introduction

The initial dissociation of CO is the most common rate-determining step in ligand substitution processes of octahedral metal carbonyls. Unlike square-planar complexes, cis labilization by the noncarbonyl substituent appears the most important factor in determining the rate of CO loss. Atwood and Brown have suggested that the labilization is mainly due to the stabilization of the transition state and have proposed a site-preference model to rationalize the experimental observations.[1]

The compound *cis*-$Ru(CO)_4(SiCl_3)_2$ is therefore remarkable in metal carbonyl chemistry in that the two carbonyls trans to the trichlorosilyl ligands undergo completely stereospecific exchange with ^{13}CO in heptane solution under mild conditions.[2] The peculiar mode of substitution has been interpreted by Atwood and Brown as being due to the high π-acceptor properties of the $SiCl_3$ group,[3] a possibility also suggested originally by Graham and co-workers.[2]

The nature of the intermediate in the exchange has been the subject of some discussion. Springer[4] has concluded that the simplest mechanisms consistent with the data for *cis*-$Ru(CO)_4(SiCl_3)_2$ were a rigid mechanism involving a square-pyramidal intermediate or a "nonrigid" mechanism involving a trigonal-bipyramidal intermediate. Graham and co-workers[2] favored the latter mechanism since such an intermediate also explained why *trans*-$Ru(CO)_4(SiCl_3)_2$ similarly gave, on ultraviolet irradiation under ^{13}CO, the stereospecifically labeled cis compound as the first product. However, it may be that the thermal exchange of the cis molecule proceeds solely by a square-pyramidal intermediate and that, in the photochemical substitution of the trans isomer, the trigonal-bipyramidal intermediate is a high-energy form which quickly rearranges to the same square-pyramidal intermediate.

It was expected that substitution of the equatorial CO groups in *cis*-$Ru(CO)_4(SiCl_3)_2$ by ligands, to give the less common *mer* isomers, would readily occur. However, the study of this compound was hampered by the tedious separation (from the trans isomer) involved in the original method of preparation.[5] This paper describes a new synthesis of *cis*-$Ru(CO)_4(SiCl_3)_2$, free from the trans form, and its extension to the iron and previously unknown osmium analogues. The reaction of these compounds (especially *cis*-$Ru(CO)_4(SiCl_3)_2$) with ligands is also reported. Part of this work has appeared in a preliminary communication.[6]

Experimental Section

General Procedure. Unless otherwise stated, reactions were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Many other manipulations such as removal of products from sublimation probes and preparation of the tetracarbonyl derivatives for microanalysis were carried out in the drybox (Vacuum Atmospheres). The ultraviolet irradiations were carried out with use of a Hanovia 200-W lamp inside a water-cooled, quartz jacket. The reactants in these reactions were contained in a cylindrical quartz tube (30 am × 3 cm diameter) fitted with a Teflon valve. The Carius tubes employed in this study were similar but were constructed of thick Pyrex glass. The high-pressure carbon monoxide investigations were performed in a 200-mL general-purpose bomb from Parr Instrument Co. Solvents were scrupulously dried, distilled, and stored under nitrogen before use. The carbonyls $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ were prepared by literature methods.[7,8] Other reagents were available commericially. Most were used without further purification except PPh_3, which was recrystallized from CH_2Cl_2/hexane, and $P(OCH_3)_3$, which was distilled from sodium under nitrogen.

Infrared spectra (Table I) were recorded with a Perkin-Elmer 237 spectrometer fitted with an external recorder. The spectra (carbonyl region) were calibrated by using carbon monoxide. Phosphorus NMR spectra (Table II) were obtained on a Varian XL 100 instrument (operating in the Fourier-transform mode, with proton decoupling) with use of CH_2Cl_2 as solvent and H_3PO_4 (85%) as an external reference (δ = 0, downfield negative). (Other NMR spectra were recorded on the same instrument.) Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer using an ionization voltage of 80 eV. (Due to the fact that ruthenium and chlorine have more than one abundant isotope, the most intense peak, in the set of peaks corresponding to the parent ion, is usually 1 mass unit higher than that calculated from atomic weights.) Microanalyses (Table I) were performed by Mr. M. K. Yang of the microanalytical laboratory of Simon Fraser University. Melting points were determined in sealed capillaries by using a Gallenkamp apparatus; they are uncorrected.

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