New Route to Complexes Having Substituted Quinoline-2-thiolate Ligands through the Metal-Assisted Coupling and Cyclization of Aryl Isothiocyanates to Alkyne Ligands

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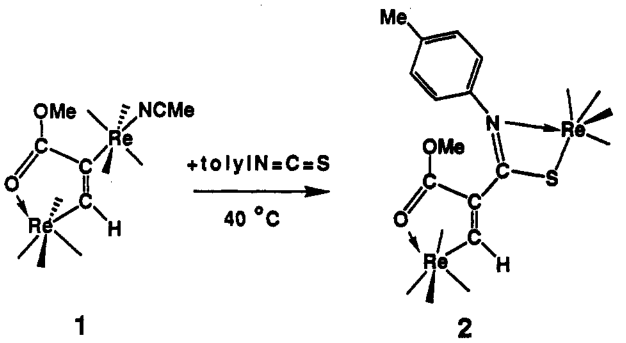
Summary: Reactions of the lightly stabilized dimetalated olefin complex $Re(CO)_4[trans\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_4(NCMe)$ *(1) with p-tolyl isothiocyanate has yielded the complex* $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)C{=}N(C_6H_4\text{-}p\text{-}Me)S]Re(CO)_4$ *(2; 58% yield) by insertion of the isothiocyanate into the substituted Re–C bond. When 2 is treated with* I_2 *in the presence of UV radiation, the tolyl ring cyclizes with the unsubstituted end of the metalated olefin to yield a new substituted quinoline-2-thiolate ligand in the complex* $Re_2(CO)_7[\mu\text{-}2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}Me\text{-}NC_9H_4](\mu\text{-}I)$ *(3; 18% yield). Complexes 2 and 3 were characterized by IR,* ^1H *NMR, and single-crystal X-ray diffraction analyses. Crystal data: for 2, space group* $P2_1/c$, $a = 10.317(1)$ Å, $b = 15.819(2)$ Å, $c = 15.448(3)$ Å, $\beta = 103.26(1)°$, $Z = 4$, *2415 reflections,* $R = 0.027$; *for* $3{\cdot}CH_2Cl_2$, $P\bar{1}$, $a = 10.204(4)$ Å, $b = 13.733(6)$ Å, $c = 9.877(2)$ Å, $\alpha = 91.18(3)°$, $\beta = 96.17(3)°$, $\gamma = 74.78(3)°$, $Z = 2$, *2746 reflections,* $R = 0.038$.

Metal complexes have been shown to be valuable agents for the activation and modification of organic isocyanates.[1] Although organic isothiocyanates are useful reagents in organic synthesis,[2] the organometallic chemistry of these molecules is not yet well developed.[3]

Recently, we have prepared the dimetalated olefin complex $Re(CO)_4[\mathit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_5$ from the reaction of the alkyne $HC{\equiv}CO_2Me$ with $Re_2(CO)_9(NCMe)$.[4] This can be converted to the more reactive compound $Re(CO)_4[\mathit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_4(NCMe)$ (1)[5] by treatment with Me_3NO in the presence of NCMe. Compound 1 has been found to produce facile head-to-tail coupling of alkynes that contain electron-withdrawing groups.[5] We have now found that complex 1 also reacts readily with *p*-tolyl isothiocyanate to yield the new complex $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)C{=}N(C_6H_4\text{-}p\text{-}Me)S]Re(CO)_4$ (2; 58% yield) by insertion of the *p*-tolyl isothiocyanate molecule into one of the rhenium–carbon bonds of the bridging alkyne ligand in 1 (eq 1).[6]



(1)

Compound 2 has been structurally characterized by X-ray diffraction methods,[7,8] and an ORTEP diagram of its molecular structure is shown in Figure 1. The molecule contains two $Re(CO)_4$ groups that are linked by an (*E*)-*N*-*p*-tolylthioamide- and methyl carboxylate-substituted vinyl grouping. The thioamido group is chelated to Re(2) (Re(2)–N = 2.178(7) Å and Re(2)–S = 2.524(3) Å). The C(2)–C(3) bond is double (1.35(1) Å), and the C(1)–C(2) bond is single (1.49(1) Å). The methyl carboxylate group is coordinated by its ketonic oxygen atom to Re(1) as in 1 (Re(1)–O(1) = 2.198(7) Å). The complex was obviously formed by the displacement of the NCMe ligand in 1 and the insertion of the isothiocyanate into the carbon-substituted metal–carbon bond in 1. Insertion of organic isothiocyanates into metal–hydrogen bonds to yield thioformamido ligands has been reported.[9] The only previous report of coupling of an organic isothiocyanate to an alkyne ligand was for the reaction of the ynamine complex $Fe_2(CO)_7(\mu\text{-}MeC_2NEt_2)$ with PhNCS to yield the complex $Fe_2(CO)_6[\mu\text{-}MeCC(NEt_2)C(S)NPh]$ (**A**), in which the carbon atom was joined to the amine-substituted carbon.[10]

When compound 2 was treated with I_2 in the presence of UV irradiation, the new complex $Re_2(CO)_7[\mu\text{-}2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}Me\text{-}NC_9H_4](\mu\text{-}I)$ (3) was obtained in 18% yield.[11] Complex 3 was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses, and an ORTEP drawing of its molecular structure is shown in Figure 2.[12] Com-

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(6) A 10.0-mg (0.014-mmol) of amount of 1 and a 10.4-mg (0.070-mmol) amount of $p\text{-}MeC_6H_4NCS$ were dissolved in 20 mL of CH_2Cl_2. The solution was heated to reflux for 3 h. After the mixture was cooled, the solvent was evaporated under vacuum, and the residue was separated by TLC by using a hexane/CH_2Cl_2 (4/1) solvent mixture to give 6.7 mg of pale yellow $Re_2(CO)_8[C(H){=}C(CO_2Me)C(S){=}NC_6H_4Me\text{-}p]$ (2; 58% yield). IR (ν_{CO} in hexane, cm^{-1}) for 2: 2099 (w), 2003 (s), 1994 (m), 1989 (m), 1952 (2), 1591 (w). ^1H NMR (δ in $CDCl_3$, ppm) for 2: 10.45 (s, 1H, C*H*), 7.04 (d, $^3J_{H\text{-}H} = 8.0$ Hz, 2H, C_6H_4), 6.73 (d, $^3J_{H\text{-}H} = 8.3$ Hz, 2H, C_6H_4), 3.48 (s, 3H, O*Me*), 2.29 (s, 3H, C_6H_4Me). Anal. Calcd (found) for 2: C, 28.92 (29.12); H, 1.33 (1.21); N, 1.69 (1.47).

(7) Crystals of 2 were grown from solution in a hexane/CH_2Cl_2 (1/1) solvent mixture at −3 °C: space group $P2_1/c$, $a = 10.317(1)$ Å, $b = 15.819(2)$ Å, $c = 15.448(3)$ Å, $\beta = 103.26(1)°$, $Z = 4$, 2415 reflections, $R = 0.027$, $R_w = 0.029$.

(8) Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. The structure solution and refinement was made by using the TEXSAN structure solving program library (v5.0) of the Molecular Structure Corp., The Woodlands, TX. An absorption correction was applied to the data.

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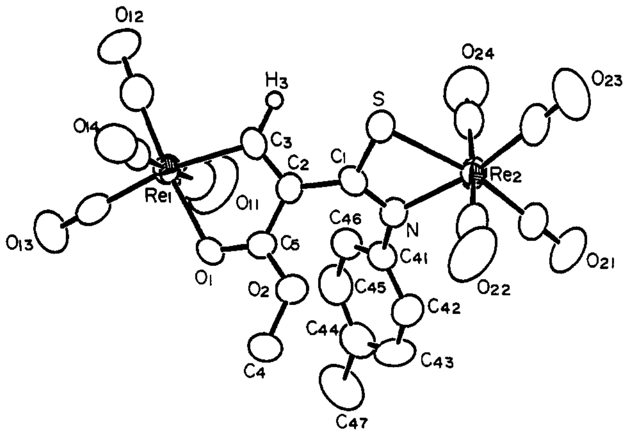


Figure 1. ORTEP diagram of $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)C{=}N(C_6H_4\text{-}p\text{-}Me)S]Re(CO)_4$ (2) showing 35% probability thermal ellipsoids. Selected interatomic distances (Å) are Re(1)–C(3) = 2.149(9), Re(1)–O(1) = 2.198(7), Re(2)–N = 2.178(7), Re(2)–S = 2.524(3), C(1)–C(2) = 1.49(1), C(2)–C(3) = 1.35(1), C(1)–N = 1.31(1), C(1)–S = 1.717(9), and C(2)–C(5) = 1.44(1).

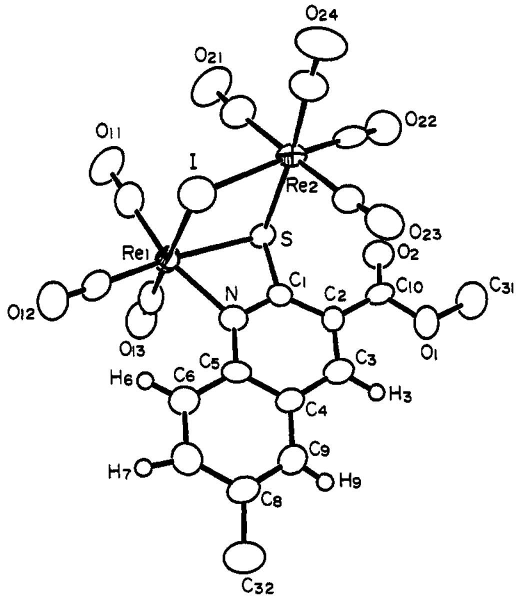
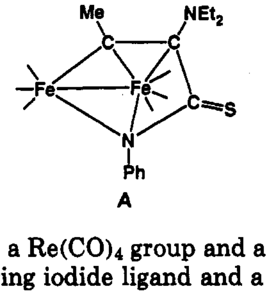


Figure 2. ORTEP diagram of $Re_2(CO)_7[\mu\text{-}2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}Me\text{-}NC_9H_4](\mu\text{-}I)$ (3) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Re(1)···Re(2) = 3.933(4), Re(1)–N = 2.20(1), Re(1)–S = 2.519(4), Re(2)–S = 2.533(4), Re(1)–I = 2.785(3), Re(2)–I = 2.803(3), C(1)–C(2) = 1.41(2), C(2)–C(3) = 1.40(2), C(1)–N = 1.33(1), C(1)–S = 1.76(1), and C(3)–C(4) = 1.41(2).



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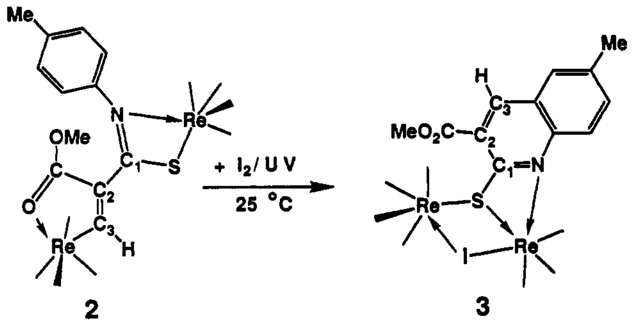
pound 3 contains a $Re(CO)_4$ group and a $Re(CO)_3$ group joined by a bridging iodide ligand and a bridging sulfur atom of a quinoline-2-thiolate ligand that contains a CO_2Me group at the 3-position and a methyl group at the 6-position. The iodide ligand serves as a three-electron donor, and the quinoline-2-thiolate ligand serves as a five-electron donor by including the two electrons being donated by the nitrogen atom that is coordinated to Re(1) (Re(1)–N = 2.20(1) Å). Both metal atoms achieve 18-electron configurations. The transformation of 2 to 3 is shown in eq 2. Compound 3 was clearly formed by the



(2)

oxidative coupling of the unsubstituted carbon of the alkenyl group in 2, C(3), to one of the ortho positions of the tolyl group. These atoms can easily approach one another by a rotation about the C(1)–C(2) single bond. One hydrogen atom of the tolyl group was eliminated, and one iodine atom was added to the complex at the metal atoms.

Photoinduced cyclization is an effective method of converting diaryl compounds into polynuclear aromatic compounds.[13] Quinoline-2-thiolate[14] and its single-ring cousin pyridine-2-thiolate[15] have recently attracted attention as ligands due to their ability to adopt several different multidentate coordination modes. By varying the substituents on the alkyne and the aryl group, it should be possible to construct a variety of new substituted quinoline-2-thiolate ligands. Efforts to achieve this are in progress.

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Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters (17 pages). Ordering information is given on any current masthead page.

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(11) A 50.0-mg (0.060-mmol) amount of 2 and a 50.0-mg (0.197-mmol) amount of I_2 were dissolved in 80 mL of hexane, and the solution was exposed to UV irradiation at 25 °C for 1 h. After the solvent was removed under vacuum, the residue was separated by TLC using a hexane/CH_2Cl_2 solvent mixture to give 3.5 mg of starting material and 10.1 mg of pale yellow $Re_2(CO)_7[\mu\text{-}2\text{-}S\text{-}CO_2Me\text{-}6\text{-}Me\text{-}NC_9H_4](\mu\text{-}I)$ (3) in 18% yield. IR (ν_{CO} in hexane, cm^{-1}) for 3: 2110 (w), 2035 (s), 2014 (m), 2003 (m), 1967 (m), 1958 (w), 1937 (m), 1925 (m), 1740 (w, br). ^{1}H NMR (δ in $CDCl_3$, ppm) for 3: 9.04 (s, 1H, C*H*), 8.12 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, C_6H_3), 7.89 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, C_6H_3), 7.79 (s, 1H, C_6H_3), 4.04 (s, 3H, O*Me*), 2.63 (s, 3H, C_6H_3Me). The mass spectrum showed the parent ion *m/e* 929 (for ^{187}Re) with ions corresponding to the loss of 1, 3, 4, 5, 6, and 7 CO ligands.

(12) Compound 3 was crystallized from a solution in CH_2Cl_2 solvent by cooling to −14 °C. Crystal data for 3·CH_2Cl_2: space group $P\bar{1}$, a = 10.204(4) Å, b = 13.733(6) Å, c = 9.877(2) Å, α = 91.18(3)°, β = 96.17(3)°, γ = 74.78(3)°, Z = 2, 2746 reflections, R = 0.038, R_w = 0.057.

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