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Synthesis of Mono- and Diiron Dithiolene Complexes as Hydrogenase Models by Dithiolene Transfer Reactions, Including the Crystal Structure of $[{Ni(S_2C_2Ph_2)}_6]$

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Supporting Information

ABSTRACT: The dithiolene transfer reaction between the nickel bis(dithiolene) complex $[Ni(S_2C_2Ph_2)_2]$ and iron carbonyls has been re-investigated, and the conditions for the production of the dinuclear product $[Fe_2(\mu-S_2C_2Ph_2)(CO)_6]$ have been optimized. Interception of a purple intermediate, thought to be [Fe- $(CO)_3(S_2C_2Ph_2)]$, in the reaction of $[Fe(CO)_5]$ with Ni- $(S_2C_2Ph_2)_2$ by the addition of PPh₃ affords the new dark blue mononuclear complex $[Fe(CO)_2(PPh_3)(S_2C_2Ph_2)]$ in good yield. The fate of the nickel dithiolene fragments in these reactions has also been established by crystallographic characterization of the hexamer $[{Ni(S_2C_2Ph_2)}_6]$ and the trinuclear cluster $[Ni_3(\mu S_2C_2Ph_2)_3(PPh_3)_2$]. The substitution reactions of $[Fe_2(\mu S_2C_2Ph_2$ (CO)₆ with PPh₃ in the presence of Me₃NO to give monosubstituted $[Fe_2(\mu-S_2C_2Ph_2)(CO)_5(PPh_3)]$ and disubstituted $[Fe_2(\mu-S_2C_2Ph_2)(CO)_4(PPh_3)_2]$ are also reported.

INTRODUCTION

It is now generally recognized that the dwindling reserves of fossil fuels and the impact of rising atmospheric CO₂ on the global climate pose a dual threat to the continued advancement of the human race. One of the most promising solutions to these problems is to use the almost inexhaustible energy source, the sun, to power the photochemical splitting of water into hydrogen and oxygen: the former could then be used as a sustainable, green fuel as the only product of its combustion is water. The development of the "hydrogen economy" faces many technological challenges, not least in its storage, transport, and efficiency of utilization; however, the effective production of dihydrogen from water remains a key problem in this endeavor. Attention has mainly focused on the reduction of protons to dihydrogen $(4H^+ + 4e^- \rightarrow 2H_2)$ rather than the associated oxidation $(2H_2O \rightarrow O_2 + 4H^+ + 4e^-)$. Although platinum is a good catalyst for this reaction, its expense and long-term unsustainability prompt the search for cheaper alternatives involving more earth-abundant metals.

Nature has solved this problem in typically efficient fashion with the evolution of hydrogenase enzymes that can catalyze the production of H₂ from protons and electrons with extremely high turnovers (>9000 s⁻¹) and low overpotentials.¹ Two types of hydrogenase, the [FeFe] and [NiFe], that occur in certain bacteria and primitive archaea are of most interest: the elucidation of the structures of their active sites (shown in Figure 1) has led to efforts by many synthetic chemists to replicate the unusual structural features and functionality involved, with some success.²





Figure 1. Structures of the dinuclear active sites of [FeFe]- and [NiFe]-hydrogenase enzymes.

Diiron complexes that contain two bridging sulfur-based ligands are very common, if not inevitable, products of the reaction of iron carbonyls with sulfur-containing reagents.⁸ Of the hundreds of hydrogenase active site models prepared, the vast majority involve compounds with this structural motif, particularly $[Fe_2(\mu$ -SCH₂XCH₂S)(CO)₆] (X = CH₂, O, NH), and their various phosphine-substituted derivatives (Figure 2).9-14 The ready accessibility of this unit also enables the incorporation of additional moieties of interest, for example, redox-active components, light-harvesting antennae, or water-solubilizing side chains. $^{15-22}$ Although a number of these systems do catalyze the production of H₂ from H⁺, they generally do so only at a large overpotential in strongly acidic

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Figure 2. Typical structures of di- and mononuclear models for the active site of the [FeFe]-hydrogenase.

solution (e.g., $HClO_4$ or $CF_3CO_2H)$ and at moderate turnover rates. $^{23-25}$

In a more recent development, several groups have explored the use of the more rigid 1,2-benzenedithiolate (bdt) or 3,4-toluenedithiolate (tdt) ligands as the bridging group.^{26–31} Moreover, mononuclear iron complexes containing these unsaturated ligands have shown good activity for catalytic proton reduction. This is particularly the case for five-coordinate complexes of the type [Fe(bdt)(CO)(L₂)], where L₂ is a diphosphine ligand (Figure 2).^{32–39} It should also be mentioned that bdt complexes of other metals, notably cobalt, nickel, and molybdenum, have also shown activity for proton reduction.^{40–45}

Over 50 years after the initial breakthroughs of the 1960s, the efficient synthesis of transition metal dithiolene complexes continues to be an important objective in inorganic chemistry.⁴⁶ We were therefore interested in exploring iron complexes similar to those in Figure 2 but containing related dithiolene ligands to take advantage of the unique properties conferred by the noninnocence of these ligands, in particular, the accessibility of a range of redox states and the possibility of incorporating additional redox-active substituents.

The bridging dithiolene complexes $[Fe_2(\mu$ -SCR¹=CR²S)-(CO)₆] 1 (Figure 3) form a subset of the class of sulfur-



Figure 3. Structure of diiron hexacarbonyl dithiolene complexes.

bridged diiron compounds. Several synthetic routes to these exist, such as the reaction of iron carbonyls with bis-(trifluoromethyl)dithiete $(R^1 = R^2 = CF_3)$,^{47,48} with dithins $(R^1 = Ph, R^2 = H \text{ or } Ph)^{49}$ or with dithioxamides $(R^1 = R^2 = NEt_2)$.⁵⁰ Alternatively the complex $[Fe_2(\mu-S_2)(CO)_6]$ can be treated with activated alkynes under UV irradiation $(R^1 = R^2 = CO_2Me, CF_3)^{51,52}$ or with the acetylide anions $R^1C\equiv C^-$ followed by protonation of the intermediates $(R^1 = H, Ph, Me, Bu, C_5H_{11}, SiMe_3, R^2 = H)$.⁵³ Schollhammer and coworkers demonstrated that one of these complexes, with $R^1 = R^2 = CO_2Me$, undergoes two reversible electrochemical reductions and is able to reduce protons catalytically.⁵²

The preparation of certain complexes of type 1 ($R^1 = R^2 = H$, Ph, Me, p-C₆H₄Me, p-C₆H₄OMe) was also reported by Schrauzer, who employed the reaction between [Fe(CO)₅] and the metal bis(dithiolenes) [M(SCR¹=CR²S)₂] (M = Fe, Co, Ni).⁵⁴ However, experimental details were rather minimal, and no yields were given. We have been studying the use of

dithiolene transfer reactions in the synthesis of both known and new dithiolene complexes for some years^{55–57} and were interested in re-investigating this route to compounds of type **1** as the availability of a large and diverse range of nickel dithiolene complexes might allow the preparation of compounds of this type that are unavailable by any of the previous routes. In this paper, we report (i) the optimization of the dithiolene transfer reaction, (ii) the modification of the synthesis to afford mononuclear phosphine-substituted complexes in one step, and (iii) the crystallographic characterization of the nickel cluster co-products of both reactions.

RESULTS AND DISCUSSION

Dithiolene Transfer Reactions: Iron Complexes. We have concentrated on the complex $[Fe_2(\mu - S_2C_2Ph_2)(CO)_6]$ (1), first, because the appropriate precursor nickel bis-(dithiolene) complex $[Ni(S_2C_2Ph_2)_2]$ is readily available and, second, because its spectroscopic data were recently reported by Mousser et al., who unexpectedly isolated it in moderate yield from the reaction of $[Fe_2(CO)_9]$ with phenyl dithiobenzoate.⁵⁸ Their paper also includes the X-ray structure determination of the complex, supplementing an earlier one by Weber and Bryan.⁵⁹

In Schrauzer's original method, the bis(dithiolene) complexes $[M(S_2C_2Ph_2)_2]$ (M = Fe, Co, Ni) were heated with a large (~20-fold) excess of $[Fe(CO)_5]$ in refluxing benzene.⁵⁴ We found that heating $[Ni(S_2C_2Ph_2)_2]$ with a 4-fold excess of $[Fe(CO)_5]$ in toluene at 80 °C overnight produced good yields of 1 (>80% based on the Ni reagent transferring one dithiolene ligand to the iron center), which can be isolated by chromatography as an air-stable bright orange-red solid and characterized by its IR, mass, ¹H, and ¹³C NMR spectra, which match those in the literature (Scheme 1).58 The reaction between $[Ni(S_2C_2Ph_2)_2]$ and $[Fe(CO)_5]$ can also be carried out at 75 °C in THF in the presence of Me₃NO (2 equiv), giving an 88% yield of 1. It is well-known that both $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ can also serve as sources of iron carbonyl fragments in reactions with sulfur-containing substrates, and as expected, the reactions of $[Ni(S_2C_2Ph_2)_2]$ with either of these reagents under similar conditions also gave good yields of 1 (72 and 98%, respectively). In all of these reactions, the only other significant product is the hexameric nickel complex 2, described later.

In most of these reactions (except, curiously, the one involving $[Fe_3(CO)_{12}])$, the reaction mixture initially changed color from green to deep purple, then gradually to orangebrown. The purple complex could not be characterized; although small amounts remained at the end of the reaction and could be collected from the chromatography column, it decomposed to a green residue when the solvent was removed. In the reaction carried out with Me₃NO, the solution rapidly turned dark purple on addition of the amine oxide, evolving gas as it did so. We consider it most likely that the purple intermediate is $[Fe(CO)_3(S_2C_2Ph_2)]$. Previously Balch and McCleverty have prepared the analogous [Fe- $(CO)_{3}$ {S₂C₂(CF₃)₂}], described as magenta;^{48,60} although it exhibited a dimeric structure in the solid state,⁶¹ it was shown to react with additional $[Fe(CO)_5]$ to give $[Fe_2(CO)_6]$ $S_2C_2(CF_3)_2$]. The only other isolable species of this type appear to be the dithiooxamide complexes $[Fe(CO)_3 \{S_2C_2\}$ $(NEt_2)_2$ and $[Fe(CO)_3{S_2C_2(NMeCH_2CH_2NMe)}]$, which undergo a similar reaction.⁵⁰ It therefore appears to be a

Scheme 1. Synthesis of the Iron Dithiolene Complexes by Dithiolene Transfer



Scheme 2. Substitution Reaction of Complex 1 with PPh₃



reasonable proposal that $[Fe(CO)_3(S_2C_2Ph_2)]$ is an intermediate in the formation of 1 in our reaction.

Both Balch and McCleverty also noted that [Fe-(CO)₃{S₂C₂(CF₃)₂}] reacted readily with phosphine ligands to give [Fe(CO)₂(L){S₂C₂(CF₃)₂}]. We therefore wondered if it would be possible to intercept the intermediate by addition of a phosphine ligand before it reacted to give 1. Addition of triphenylphosphine to the dark purple solution produced from [Ni(S₂C₂Ph₂)₂] and 1 equiv of [Fe(CO)₅] in the presence of Me₃NO caused an immediate color change to green, and the dark blue substituted complex [Fe(CO)₂(PPh₃)(S₂C₂Ph₂)] **3** (vide infra) was isolated in 59% yield (Scheme 1). Hence, the purple intermediate certainly reacts as if it were [Fe-(CO)₃(S₂C₂Ph₂)], and we are currently exploring this procedure as a useful route to other mononuclear iron carbonyl dithiolene derivatives.

Substitution Reactions of 1 ($\mathbb{R}^1 = \mathbb{R}^2 = \mathbb{Ph}$) with PPh₃. No reaction occurred on stirring a dichloromethane solution of 1 ($\mathbb{R}^1 = \mathbb{R}^2 = \mathbb{Ph}$) with 1 or 2 equiv of PPh₃ at room temperature. However, on addition of 1 or 2 equiv of Me₃NO, the solution darkened rapidly and three products could be isolated by column chromatography or TLC: the red monosubstituted complex [Fe₂(μ -S₂C₂Ph₂)(CO)₅(PPh₃)] 4, the brown disubstituted complex [Fe₂(μ -S₂C₂Ph₂)-(CO)₄(PPh₃)₂] 5, and the blue mononuclear species [Fe $(CO)_2(PPh_3)(S_2C_2Ph_2)$] 3 (Scheme 2). Compound 5 is airsensitive and decomposes to 3 during purification, but this does not account for the total amount of this product: it is already present in the reaction mixture before workup. Compounds 3-5 were readily characterized by their spectroscopic data and by comparison to other related species. For example, Dixneuf and co-workers have previously shown that the analogous disubstituted tetrathiooxalate complexes $[Fe_2\{\mu-S_2C_2(SR)_2\}(CO)_4(PPh_3)_2]$ (R = Me, Et), prepared by reduction of $[Fe(CO)_2(PPh_3)_2(CS_2R)]^+$, also decompose to $[Fe{S_2C_2(SR)_2}(CO)_2(PPh_3)]$ on exposure to air; they also crystallographically characterized both the dinuclear and mononuclear products for $R = Me.^{62}$ Numerous mono- and disubstituted derivatives of the toluene-dithiolate complex $[Fe_2(\mu-S_2C_6H_3Me)(CO)_6]$ and the 1,3-propanedithiolate complex $[Fe_2(\mu-S_2C_3H_6)(CO)_6]$ with PPh₃ have been prepared and structurally characterized.^{10,26,27} By analogy with these compounds, we expect the phosphine ligands to occupy the apical positions in 4 and 5, as shown in Scheme 2.62,6

The crystal structure of mononuclear complex 3 was determined and is shown in Figure 4, with bond lengths and angles summarized in the caption. The complex is best described as adopting a square-based pyramidal geometry with the phosphine ligand in the apical position; the trigonality



Figure 4. Molecular structure of $[Fe(CO)_2(PPh_3)(S_2C_2Ph_2)]$ 3 in the crystal. Selected bond lengths (Å) and angles (deg): Fe(1)-S(1) 2.1761(5), Fe(1)-S(2) 2.1942(5), Fe(1)-P(1) 2.2158(6), Fe(1)-C(33) 1.791(2), Fe(1)-C(34) 1.791(2), C(33)-O(1) 1.142(2), C(34)-O(2) 1.142(2), C(1)-C(2) 1.371(3); S(1)-Fe(1)-S(2) 88.18(2), S(1)-Fe(1)-P(1) 113.52(2), S(2)-Fe(1)-P(1) 94.05(2), C(33)-Fe(1)-S(1) 84.57(6), C(33)-Fe(1)-S(2) 167.01(6), C(33)-Fe(1)-P(1) 98.72(6), C(33)-Fe(1)-C(34) 91.27(9), C(34)-Fe(1)-S(1) 152.59(6), C(34)-Fe(1)-S(2) 90.23(6), C(34)-Fe(1)-P(1) 93.89(6).

index, τ , was 0.24.⁶⁴ Interestingly, this is subtly different from the structure of $[Fe{S_2C_2(SMe)_2}(CO)_2(PPh_3)]$, which, although still square-based pyramidal with $\tau = 0.29$, had a CO ligand as the apical group.⁶² The origin of this difference may be steric, as it places the bulky phosphine ligand further away from the diphenyldithiolene. It has been known for many years that a similar ruthenium complex, $[Ru(CO)-(PPh_3)_2\{S_2C_2(CF_3)_2\}]$, exists as two interconverting square pyramidal isomers: one violet with an apical phosphine ligand and the other orange with the CO ligand in the apical position; very recently, the two forms have been shown to interconvert via an observable trigonal bipyramidal intermediate.^{48,65–68}

In a very recent paper, a contrasting result to ours was obtained by Mousser and co-workers.⁶⁹ Treatment of 1 with $P(OMe)_3$ in toluene at 45 °C gave mono- and disubstituted dinuclear species analogous to 4 and 5, but instead of a monosubstituted analogue of 3, the disubstituted mononuclear complex $[Fe(CO){P(OMe)_3}_2(S_2C_2Ph_2)]$ was obtained. This compound adopts a structure somewhat more toward trigonal bipyramidal ($\tau = 0.44$) in which both phosphite ligands occupy equatorial positions, the dithiolene ligand spans the axial and equatorial sites, and the CO is in the remaining axial position. Clearly, the ligand arrangement in these mononuclear species

is very dependent on the steric and electronic properties of the ligands concerned. Our attempts to induce a second substitution in $[Fe(CO)_2(PPh_3)(S_2C_2Ph_2)]$ were hampered by the fact that heating the complex in refluxing toluene, either alone or with PPh₃, unexpectedly caused its almost quantitative transformation into the known bis(dithiolene) complex $[Fe(PPh_3)(S_2C_2Ph_2)_2]$.^{54,70} In contrast, $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]$ is known to undergo a second phosphine substitution reaction under thermal conditions to give $[Fe(CO)(L)_2\{S_2C_2(CF_3)_2\}]$.^{48,60}

Because it appeared that 1 may be formed by the reaction of $[Fe(CO)_3(S_2C_2Ph_2)]$ with additional $[Fe(CO)_5]$, we also attempted to prepare the monosubstituted complex 4 by the reaction of complex 3 with an excess of $[Fe(CO)_5]$ and Me₃NO. Although 4 was formed in 39% yield, the major product was the unsubstituted complex 1 (51%). No trace of the purple band that we propose to be $[Fe(CO)_3(S_2C_2Ph_2)]$ was observed in this reaction; it therefore seems likely that the initial product is indeed 4, but the PPh₃ ligand is then replaced by CO to give 1.

The electrochemical behavior of 1 was reported recently.⁶⁹ The cyclic voltammogram of complex 3 is shown in Figure 5. The compound displays a reversible reduction wave at -1.359



Figure 5. Cyclic voltammogram of complex 3 in CH_2Cl_2 solution (room temperature, scan rate 100 mV s⁻¹).

V (vs Fc/Fc^+) as well as some more complex oxidation behavior. Addition of successive 100 equiv aliquots of acetic acid did cause a small but consistent increase in the current of the reduction wave (see Supporting Information), but we conclude that the ability of 3 to catalyze the proton reduction reaction under these conditions is weak at best.

Dithiolene Transfer Reactions: Nickel Complexes. In addition to the iron complexes produced in the dithiolene transfer reactions, we have also characterized the nickel clusters that occur as co-products. In all of the dithiolene transfer reactions giving 1, the brown complex $[{Ni}(S_2C_2Ph_2)]_6]$ 2 was

eluted as a co-product in a yield similar to that of 1 (when calculated on the basis of the starting nickel complex). It therefore appears that only one dithiolene ligand from the nickel starting material is transferred to the iron center, and the remaining $Ni(S_2C_2Ph_2)$ fragments assemble into the hexamer. This compound, formulated at the time as $[{Ni(S_2C_2Ph_2)}_n]$, was first isolated in the 1960s by Schrauzer in the reactions of $[Ni(S_2C_2Ph_2)_2]$ with alkynes. It was suggested that only one dithiolene ligand per complex reacted (to give thiophenes), leaving the remaining $Ni(S_2C_2Ph_2)$ fragment to associate into a brown complex that they initially described as a tetramer (n =4).⁷¹⁻⁷³ In the following year, they isolated the same compound as a byproduct in dithiolene transfer reactions between $[Ni(S_2C_2Ph_2)_2]$ and $[M(CO)_6]$ (M = Cr, Mo, W);⁷⁴ much later, Holm and co-workers also observed it in the related reaction of $[Ni(S_2C_2Ph_2)_2]$ with $[M(CO)_3(NCMe)_3]$ (M = Mo, W) and described it as probably polymeric.^{75,76} The reaction of $[Ni(S_2C_2Ph_2)_2]$ with nickelocene to give [CpNi- $(S_2C_2Ph_2)$] also produced complex 2, and in this case, an ion was observed in the mass spectrum at m/z 1806, indicating a hexameric structure.⁷⁷ We have previously observed its formation in reactions of $[Ni(S_2C_2Ph_2)_2]$ with carbonylcontaining substrates,⁵⁵ though interestingly, in other cases involving dithiolene transfer to complexes containing halides (such as [CpMo(CO)₃Cl] or [RuCl₂(PPh₃)₃]), it was not produced, and the fate of the nickel in these reactions remains unclear.^{56,5}

Bis- or trisdithiolene complexes of the general formula $[M(S_2C_2R_2)_2]$ or $[M(S_2C_2R_2)_3]$ are relatively common and can be prepared for most of the transition metals.⁴⁶ However, monodithiolene complexes of the general type $[M(S_2C_2R_2)]_n$ with a 1:1 metal/dithiolene ratio are much rarer and are



Figure 6. Molecular structure of complex 2 in the crystal.



Figure 7. Schematic view of the framework of cluster 2 from the side (left) and top (right) of the molecule.

confined to four structurally characterized compounds: the dimeric $[{Tl(bdt)}_2]^{2-}$ (bdt = 1,2-benzenedithiolate, $S_2C_6H_4$),⁷⁸ the tetramer $[{Ag(mnt)}_4]^{4-}$, mnt = 1,2-maleoni-triledithiolate, $S_2C_2(CN)_2$,⁷⁹ and two hexameric palladium complexes discussed in more detail below. It was therefore of interest to structurally characterize **2**, which is the most readily available member of this series.

Crystallization of 2 was effected by diffusion of light petroleum into a dichloromethane solution at room temperature, giving brown needles. The structure is depicted in Figure 6 and is based on an octahedral arrangement of six nickel atoms, each of which is in a square planar coordination environment; if an imaginary cube is constructed such that the nickel atoms lie in the centers of its faces, the sulfur atoms of the dithiolene ligands occupy the centers of each edge of this cube. Unique nickel atom Ni(1) at the top of the diagram bears two chelating dithiolene ligands, the sulfur atoms of which each bridge to one of the four nickel atoms in the equatorial positions [Ni(3)-Ni(6)]. The other unique nickel atom, Ni(2), at the bottom of the octahedron is bonded to four different dithiolene ligands, each of which bridges to one of the equatorial nickels, which are themselves therefore ligated by three different dithiolenes. All of the Ni-Ni distances are greater than 3.0 Å, precluding any significant metal-metal bonding. The Ni-S distances within a chelating dithiolene ring lie in the range of 2.16-2.19 Å, whereas the bridging Ni-S distances are longer, between 2.23 and 2.27 Å.

Two closely related hexanuclear palladium dithiolene complexes have been described. The first of these, [Pd- $\{S_2C_2(CO_2Me)_2\}]_6$, was isolated by Stiefel from the reaction of [PdCl₂(NCMe)₂] with [Zn(tmeda) $\{S_2C_2(CO_2Me)_2\}$.⁸⁰ Its structure consists of an octahedral Pd₆ core bridged by dithiolene ligands but in a subtly different way such that the structure has S₆ symmetry and each Pd is bonded to three different dithiolene ligands. More recently, Rawson and co-workers explored the oxidative addition of tetrathiocins to Pd(0) complexes, producing the benzenedithiolate cluster [Pd $\{S_2C_6H_2(OMe)_2\}$]₆, which has the same arrangement of the dithiolate ligands as in **2**.⁸¹

In the solid-state structure of 2, there is a two-fold axis of symmetry which renders pairs of dithiolene ligands equivalent; within each dithiolene ligand, the two carbons are not equivalent. In the ¹³C NMR spectrum, one would therefore expect to see six signals of equal intensity for the dithiolene carbons and the same for the *ipso* carbons of the phenyl substituents. A total of 12 signals are observed in this region, implying that the solid-state structure is maintained in solution.

The molecule is chiral: as shown in Figure 7, when viewed from above Ni(1), the dithiolene ligands of each sulfur in the equatorial plane bridge to the nickel atom in a leftward direction, whereas its enantiomer would have the opposite direction (the molecule of Rawson's Pd₆ complex depicted in that paper is the right-handed enantiomer).⁸¹

The cyclic voltammogram of hexamer **2** is shown in Figure 8. The complex displays two reversible reduction waves at



Figure 8. Cyclic voltammogram of complex 2 in CH_2Cl_2 solution (room temperature, scan rate 100 mV s⁻¹).

-1.028 and -1.593 V (vs Fc/Fc⁺) as well as two smaller oxidation waves at 0.277 and 0.470 V, followed by a larger wave (which may consist of two closely spaced oxidations) at 0.962 V. It is interesting to note that Stiefel's [Pd-{S₂C₂(CO₂Me)₂}]₆ cluster showed four reversible reduction waves, whereas Rawson's Pd₆ cluster showed only two reductions and two oxidations (the oxidation behavior of Stiefel's cluster was not reported).^{80,81}

The reactions carried out in the presence of PPh₃ to give 3 did not, however, produce the hexamer 2. Instead, a new cluster, $[Ni_3(\mu$ -S₂C₂Ph₂)₃(PPh₃)₂] 6 (Figure 9), was isolated in low yield as a green solid; its mass spectrum showed a molecular ion centered on m/z 1426. The single-crystal X-ray structure of this complex is shown in Figure 10, with important bond lengths and angles detailed in the caption. The structure consists of an equilateral triangle of nickel atoms; Ni(1) and Ni(2), each of which bears a phosphine ligand are symmetri-



Figure 9. Structure of $[Ni_3(\mu - S_2C_2Ph_2)_3(PPh_3)_2]$ 6.

cally bridged by sulfur atoms S(5) and S(6) of the unique dithiolene ligand. In contrast, Ni(3) is ligated by two chelating dithiolenes, which are bridging in the unusual μ_3 coordination mode: one sulfur of each ligand bridges to Ni(1) and the other to Ni(2). The bridging of these two dithiolenes is much more asymmetric: the average Ni(3)-S distance is 2.162 Å, whereas the average Ni(1)/Ni(2) bond distance to the same four sulfurs is 2.2905 Å. The geometry about Ni(3) is thus distorted square planar, whereas the other two metals have a square pyramidal coordination environment. Although the cluster has 52 electrons as opposed to the more usual 48 (which corresponds to an 18 electron configuration for each metal with three M-M single bonds), the three Ni-Ni distances are all similar [2.4914(7)-2.5305(9) Å] and well within the range observed for a bonding interaction, and the Ni-Ni-Ni angles are close to 60° . The μ_3 coordination of the dithiolene ligand, in which the ligand largely retains its planarity, has been



Figure 10. Molecular structure of complex **6** in the crystal. Selected bond lengths (Å): Ni(1)–Ni(2) 2.4914(7), Ni(1)–Ni(3) 2.5125(8), Ni(2)–Ni(3) 2.5305(9), Ni(2)–S(1) 2.4767(12), Ni(3)–S(1) 2.1566(13), Ni(2)–S(2) 2.4500(14), Ni(3)–S(2) 2.1629(12), Ni(1)–S(3) 2.4959(12), Ni(3)–S(3) 2.1621(11), Ni(1)–S(4) 2.4147(13), Ni(3)–S(4) 2.1657(13), Ni(1)–S(5) 2.2840(13), Ni(2)–S(5) 2.2883(12), Ni(1)–S(6) 2.2975(13) Ni(2)–S(6) 2.2924(12), Ni(1)–P(2) 2.2720(11), Ni(2)–P(1) 2.2759(12), C(19)–C(20) 1.356(6), C(65)–C(66) 1.344(6), C(51)–C(52) 1.374(8).

observed previously in mixed-metal clusters by Nishihara.^{82,83} Moreover, two structurally very similar benzenedithiolate clusters, $[\rm Ni_3(\mu\text{-bdt})_3(\rm PPh_3)_2]$ and $[\rm Ni_3(\mu\text{-bdt})_3(\rm PPh_2Me)_2]$, both of which also feature relatively short Ni–Ni distances, have been reported in the literature.^{84,85}

Cluster 6 is evidently formed by the interception of the $Ni(S_2C_2Ph_2)$ units produced in the dithiolene transfer reaction by PPh₃, thus preventing them from associating further into hexamer 2. This suggests that a general route to such compounds might involve generating such units in the presence of other phosphines, a possibility we are currently exploring.

CONCLUSIONS

We have confirmed that the dithiolene transfer reaction of $[Ni(S_2C_2Ph_2)_2]$ with iron carbonyls forms a viable route to the dinuclear complex $[Fe_2(\mu-S_2C_2Ph_2)(CO)_6]$, as described by Schrauzer. Furthermore, we have demonstrated that the reaction passes through an intermediate species, thought to be $[Fe(CO)_3(S_2C_2Ph_2)]$, that can be intercepted by reaction with PPh₃ to give useful yields of $[Fe(CO)_2(PPh_3)(S_2C_2Ph_2)]$ in a convenient one-pot synthesis. We are currently exploring the scope of this reaction with other dithiolene ligands and phosphines and studying the electrochemical and catalytic properties of the resulting five-coordinate complexes.

In addition, we have also structurally characterized the hexameric nickel co-product $[{Ni(S_2C_2Ph_2)}_6]$ **2**, a compound commonly observed in dithiolene transfer reactions. More unexpectedly, we have shown that, in the presence of PPh₃, the aggregation of the Ni(dithiolene) fragments can be arrested before they form **2**, giving instead a new trinuclear cluster **6**; in this way, it may be possible to synthesize a range of different clusters of intermediate nuclearity by the addition of different ligands.

EXPERIMENTAL SECTION

All reactions were performed under an inert atmosphere of argon or nitrogen using Schlenk techniques. Solvents for reactions were purified with a Grubbs-type purification system manufactured by Innovative Technology, Newburyport, MA. Chromatographic separations were carried out on Geduran 60 silica under a positive pressure of nitrogen; columns were initially made up in light petroleum (40-60 °C fraction); polarity was increased by addition of increasing proportions of dichloromethane. The ¹H (400 MHz), ¹³C NMR (100 MHz), and ³¹P NMR (162 MHz) spectra were obtained in CDCl₃ solution on a Bruker Avance AVIIIHD machine having an automated sample changer. Chemical shifts are given on the δ scale relative to SiMe₄ for ¹H and ¹³C and relative to 85% H₃PO₄ for ³¹P. The ¹³C{¹H} NMR spectra were routinely recorded using an attached proton test technique (JMOD or DEPT-Q pulse sequence). Mass spectra were recorded on Waters LCT instruments operating in electrospray (ES⁺) or atmospheric pressure chemical ionization (AP⁺) mode. Solid-state IR spectra were recorded neat with a diamond ATR device over the range of 4000-400 cm⁻¹ and solution spectra in CH_2Cl_2 solution over the range of 2200–1550 \mbox{cm}^{-1} on a PerkinElmer Spectrum Two instrument. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry.

Standard cyclic voltammetry was carried out using an Autolab Potentiostat 100 attached to a computer using NOVA 1.10.5 software to record the data. The data were processed using OriginPro 2018. The experiments were performed at room temperature in a glass sample tube using a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode under a nitrogen atmosphere. The solvent was dichloromethane containing $[\rm NBu_4][\rm PF_6]$ (0.4 M) as supporting electrolyte. The compound concentration was 2 mM unless stated otherwise. The solution was saturated with N₂ by bubbling the gas into the solution for a minimum of 10 min. All redox potentials quoted in the figures and results and discussion sections are versus the ferrocene/ferrocenium couple (Fc/Fc⁺). Scan rates of 20–500 mVs⁻¹ were used, with the figure caption stating which was used to obtain the traces shown.

All chemicals were purchased from Sigma-Aldrich UK with the exception of $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$, which were previously synthesized laboratory stock. Commercial Me₃NO·2H₂O was rendered anhydrous by azeotropic distillation in toluene and stored under argon. The complex $[Ni(S_2C_2Ph_2)_2]$ was prepared by the literature method.⁷¹

Caution. Although we have no evidence for the formation of highly toxic $[Ni(CO)_4]$ during these reactions, this possibility should be borne in mind during workup.⁸⁶

Synthesis of $[Fe_2(\mu-S_2C_2Ph_2)(CO)_6]$ (1; $R^1 = R^2 = Ph$). A solution of $[\rm Ni(S_2C_2Ph_2)_2]$ (0.7713 g, 1.41 mmol) in toluene (50 cm^3) was treated with $[Fe(CO)_5]$ (0.68 cm^3 , 5.03 mmol) and heated to 80 °C for 23 h in a thermostatically controlled oil bath. The initially green solution rapidly became dark purple and then more slowly changed to an orange-red color. After cooling to rt and addition of silica (about 5 g), the solvent was removed in vacuo. The solid was then loaded onto a chromatography column. Elution with light petroleum/CH2Cl2 (9:1) produced an orange-red band of product 1 (0.6061 g, 1.16 mmol, 82% based on Ni). Elution with a 4:1 mixture of the same solvents gave an unidentified purple band, which turns green on removal of the solvent, and with a 3:2 mixture, a small band of starting nickel complex was eluted. Continued elution with a 2:3 mixture of these solvents gave a brown band due to $[{Ni(S_2C_2Ph_2)}_6]$ 2 (0.3958 g, 0.219 mmol, 93% based on Ni). Two further minor bands could be eluted with a 7:3 mixture of the same solvents but remain unidentified.

Alternatively, a solution of $[Ni(S_2C_2Ph_2)_2]$ (0.7096 g, 1.30 mmol) and $[Fe(CO)_5]$ (0.68 cm³, 5.03 mmol) in THF (100 cm³) was treated with Me₃NO (0.7896 g, 10 mmol). The green solution immediately turned purple, accompanied by gas evolution. It was then heated at 75 °C for 23 h. Chromatographic workup as above gave 1 (0.5968 g, 1.14 mmol, 88% based on Ni).

Data for 1: IR (hexane) 2077m, 2042s, 2005vs, 1990w cm⁻¹; ¹H NMR δ 7.20, 7.02 (m, Ph); ¹³C NMR δ 207.8 (CO), 150.2 (CPh), 135.1 (C_{ipso}), 128.9, 128.5, 127.3 (Ph); mass spectrum *m*/*z* 523 (M + H)⁺. These data are in agreement with those reported previously.¹²

Data for 2: IR (ATR) 3054w, 2953w, 1594w, 1483w, 1441w, 1175w, 1074w, 1029w, 761m, 738s, 692vs cm⁻¹; ¹H NMR δ 7.54–6.98 (m, Ph); ¹³C NMR δ 145.7, 144.6, 141.6, 141.5, 141.4, 140.0, 138.6, 138.5, 138.4, 138.4, 138.0, 137.6 (CPh + C_{ipso}), 130.2–125.3 (m, Ph); mass spectrum (ES⁺) m/z 1804. Anal. Calcd for C₈₄H₆₀Ni₆S₁₂·2CH₂Cl₂: C, 52.27; H, 3.24; S, 19.45. Found: C, 52.43; H, 3.59; S, 18.84%.

Synthesis of $[Fe_2(\mu-S_2C_2Ph_2)(CO)_6]$ (1; $R^1 = R^2 = Ph$) from $[Fe_2(CO)_9]$ or $[Fe_3(CO)_{12}]$. A solution of $[Ni(S_2C_2Ph_2)_2]$ (0.8917 g, 1.64 mmol) and $[Fe_2(CO)_9]$ (1.1897 g, 3.27 mmol) in toluene (50 cm³) was heated to 80 °C for 24 h. The color of the solution changed rapidly to purple and ultimately orange-red as before. Separation of the products by column chromatography as above produced 1 (0.6179 g, 1.18 mmol, 72% based on Ni). In a similar way, a solution of $[Ni(S_2C_2Ph_2)_2]$ (0.7462 g, 1.37 mmol) and $[Fe_3(CO)_{12}]$ (0.9010 g, 1.78 mmol) in toluene (50 cm³) was heated at 80 °C for 24 h. In this case, the solution did not pass through a purple stage but slowly turned to dark orange-red. The product 1 was isolated as above (0.7017 g, 1.34 mmol, 98% based on Ni).

Synthesis of $[Fe(CO)_2(PPh_3)(S_2C_2Ph_2)]$ 3 from $[Fe(CO)_5]$. A solution of $[Ni(S_2C_2Ph_2)_2]$ (0.5086 g, 0.937 mmol) and $[Fe(CO)_5]$ (0.15 cm³, 1.09 mmol) in THF (100 cm³) was treated with Me₃NO (0.135 g, 1.76 mmol). A rapid color change to dark purple occurred. The solution was stirred for 15 min, then triphenylphosphine (0.2800 g, 1.07 mmol) was added, causing a further change to green. The solution was stirred overnight to ensure complete reaction. After addition of silica (5 g), the solvent was removed in vacuo and the

residue loaded onto a column. Elution with light petroleum/CH₂Cl₂ (9:1) produced an orange-red band of 1 (30.1 mg, 0.06 mmol) and a purple band, which was followed by a green band of residual $[Ni(S_2C_2Ph_2)_2]$ (41.7 mg, 8% recovery), eluted with a 17:3 mixture of the same solvents. The major dark blue band of **3** was then eluted with a 3:1 mixture of the same solvents; the compound was recolumned to remove the last traces of $[Ni(S_2C_2Ph_2)_2]$, giving a final yield of 341.9 mg (0.51 mmol, 59% based on Ni). When the reaction was repeated with 1 equiv of Me₃NO, a slightly lower yield of 54% was obtained.

After the elution of the major product, the green complex $[Ni_3(\mu S_2C_2Ph_2)_3(PPh_3)_2]$ 6 could be eluted with a mixture of $CH_2Cl_2/$ acetone (19:1). It proved difficult to obtain this complex in a pure state due to persistent contamination by $Ph_3P=O$ and $Ph_3P=S$ impurities, but washing with ethyl acetate followed by crystallization gave a solid in which they were absent in the mass spectrum. The yield so obtained was 70 mg (16%). Solutions gradually turn brown and decompose on exposure to air.

Data for 3: IR (CH₂Cl₂) 2006s, 1952s cm⁻¹; ¹H NMR δ 7.73–7.07 (m, Ph); ¹³C NMR δ 212.4 (d, J = 10 Hz, CO), 168.9 (CPh), 142.4 (C_{ipso} of Ph), 133.3–127.1 (m, Ph); ³¹P NMR δ 67.6; mass spectrum m/z 617 (M + H)⁺. Anal. Calcd for C₃₄H₂₅FeO₂S₂P: C, 66.23; H, 4.06; S, 10.39. Found: C, 65.70; H, 4.17; S, 10.29%.

Data for 6: ¹H NMR δ 7.35–6.82 (m, 58 H, Ph), 6.51 (d, 2 H, Ph); ¹³C NMR δ 171.5 (CPh), 150.2, 142.2, 141.2, 140.1 (CPh + C_{ipso}), 134.6 (Ph), 131.2 (C_{ipso}), 130.5–125.9 (m, Ph); ³¹P NMR δ 43.3 (s, br); mass spectrum (ES⁺) m/z 1426 (M⁺); HRMS found m/z1426.0485; calcd for C₇₈H₆₀Ni₃P₂S₆ m/z 1426.0528.

Reaction of $[Fe_2(\mu \cdot S_2C_2Ph_2)(CO)_6]$ (1; $R^1 = R^2 = Ph$) with PPh₃. A solution of $[Fe_2(\mu \cdot S_2C_2Ph_2)(CO)_6]$ (0.5229 g, 1.00 mmol) and triphenylphosphine (0.573 g, 2.18 mmol) in dichloromethane (110 cm³) was treated with Me₃NO (0.158 g, 2.10 mmol) and allowed to stir at room temperature for 19 h. The solvent was removed in vacuo and the residue absorbed onto silica and loaded onto a column. Elution with light petroleum/CH₂Cl₂ (9:1) gave a red band of the monosubstituted complex $[Fe_2(\mu \cdot S_2C_2Ph_2)-(CO)_5(PPh_3)]$ 4 (514.0 mg, 0.67 mmol, 67%). Elution with a 4:1 mixture of the same solvents gave a blue band due to the mononuclear complex $[Fe(S_2C_2Ph_2)(CO)_2(PPh_3)]$ 3 (70.0 mg, 0.11 mmol, 11%). This was followed by a brown band of the disubstituted complex $[Fe_2(\mu \cdot S_2C_2Ph_2)(CO)_4(PPh_3)_2]$ 5 (173.0 mg, 0.175 mmol, 17.5%), eluted with a 3:1 mixture of the same solvents.

Data for 4: IR (hexane) 2052vs, 1996vs, 1985m, 1947w cm⁻¹; ¹H NMR δ 7.67 (t, *J* = 9.0 Hz, 6 H), 7.32 (m, 9 H), 7.10 (t, *J* = 7.2 Hz, 2 H), 7.02 (t, *J* = 7.4 Hz, 4 H), 6.63 (d, *J* = 7.5 Hz, 4 H); ¹³C NMR δ 214.1 (d, *J* = 8 Hz, 2CO), 209.7 (3CO), 149.7 (CPh), 136.2 (d, *J* = 40 Hz, C_{ipso} of PPh₃), 136.0 (C_{ipso}), 133.6–127.8 (m, Ph); ³¹P NMR δ 61.6; mass spectrum m/z 757 (M + H)⁺. Anal. Calcd for C₃₇H₂₅Fe₂O₅S₂P: C, 58.73; H, 3.31; S, 8.47. Found: C, 58.57; H, 3.34; S, 8.22%.

Data for **5**: IR (CH₂Cl₂) 2000vs, 1954m, 1938s cm⁻¹; ¹H NMR δ 7.61 (t, J = 8.7 Hz, 12 H), 7.25 (m, 20 H), 6.94 (t, J = 7.4 Hz, 2H), 6.79 (t, J = 7.6 Hz, 4 H), 6.31 (d, J = 7.5 Hz, 4 H); ¹³C NMR δ 215.7 (t, J = 4 Hz, CO), 148.8 (CPh), 136.8 (d, J = 38 Hz, C_{ipso} of PPh₃), 136.4 (C_{ipso} of Ph), 133.5–127.0 (m, Ph); ³¹P NMR δ 58.4; mass spectrum m/z 991 (M + H)⁺. Anal. Calcd for C₅₄H₄₀Fe₂O₄S₂P₂· 1.5CH₂Cl₂: C, 59.60; H, 3.85; S, 5.73. Found: C, 59.64; H, 4.08; S, 5.72%.

Reaction of $[Fe(CO)_2(PPh_3)(S_2C_2Ph_2)]$ 3 with $[Fe(CO)_5]$ and Me_3NO . A solution of $[Fe(CO)_2(PPh_3)(S_2C_2Ph_2)]$ (99.8 mg, 0.162 mmol) in THF (10 cm³) was treated with $[Fe(CO)_5]$ (0.1 cm³, 0.76 mmol) and Me_3NO (61.3 mg, 0.82 mmol). A rapid color change occurred to murky green-brown. After being stirred for 18 h, the solution was brown. Separation of the mixture by column chromatography gave an orange band due to 1 (43.3 mg, 0.083 mmol, 51%), eluted with light petroleum/CH₂Cl₂ (19:1); a red band due to 4 (48.5 mg, 39%) eluted with a 17:3 mixture of the same solvents, and a small amount of remaining 3 eluted with a 7:3 ratio of the same solvents.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00852.

¹H, ¹³C and ³¹P NMR spectra and selected mass spectra of compounds reported in this paper, with summary tables of crystal data for complexes **2**, **3**, and **6** (PDF)

Accession Codes

CCDC 1878620–1878622 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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