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The synthesis of *cis*- $\text{Re}(O, O'-\text{NO}_2)(\text{CO})_2(\text{PPh}_3)_2$ containing the unusual *O, O'*-chelating nitrite ligand and its reaction with CO. Evidence for a rhenium–nitrogen interaction

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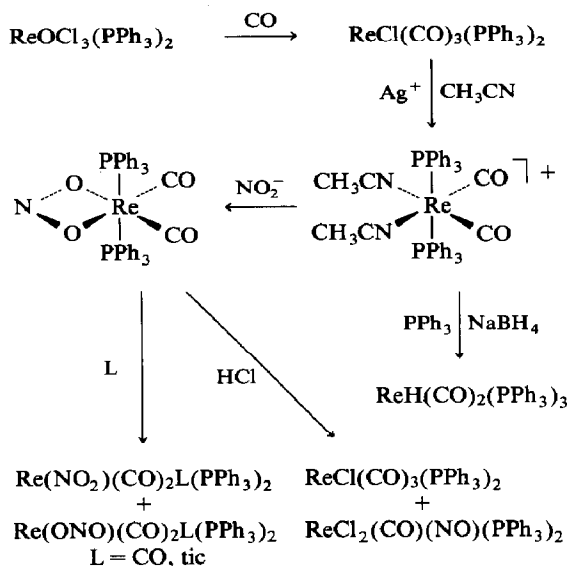
Abstract

The synthesis of the bidentate nitrite complex, $\text{Re}(O, O'-\text{NO}_2)(\text{CO})_2(\text{PPh}_3)_2$, from $[\text{Re}(\text{CH}_3\text{CN})_2(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$ is reported. The possibility of a Re–N interaction in $\text{Re}(O, O'-\text{NO}_2)(\text{CO})_2(\text{PPh}_3)_2$ is indicated by the derivative chemistry of the complex with CO, *p*-tolylisocyanide and HCl. A superior, high yield route to $\text{ReH}(\text{CO})_2(\text{PPh}_3)_3$ is also described.

Introduction

For several years now we have been investigating the coordination chemistry of nitrosyl rhenium complexes. Our efforts have largely concentrated on exploring derivatives of $\text{ReH}_2(\text{NO})(\text{PPh}_3)_3$ [1], which is a particularly convenient precursor [2–4]. There are, however, many other methods available for the synthesis of nitrosyl complexes [5]. Of these, oxygen atom transfer from coordinated nitrite to carbon monoxide or tertiary phosphine represents a clean and direct method of introducing the nitrosyl group [6], with the added attraction of effecting a two electron reduction of the metal centre at the same time. For this reason, we set out to synthesize and investigate the chemistry of selected nitrite complexes of rhenium, with a view towards generating routes to various members of the series $\text{Re}(\text{NO})(\text{CO})\text{L}(\text{PPh}_3)_2$.

In this paper we report the synthesis of the unusual bidentate nitrito complex, $\text{Re}(O, O'-\text{NO}_2)(\text{CO})_2(\text{PPh}_3)_2$, which, although proving of little use as a nitrosyl precursor, did prove to possess interesting chemistry of its own, some of it suggesting the possibility of a rhenium–nitrogen interaction in the complex. The various complexes reported in this paper and their derivatives are depicted in Scheme 1.



Scheme 1

Experimental section

CAUTION! *Compound 1* should be treated with the extreme caution normally afforded for organometallic perchlorate salts, which are potentially explosive [7].

Although we have not experienced any difficulties with the handling of this compound, it is advisable to minimize the potential hazards by observing the following simple precautions: (i) Keep reaction scales small. (ii) Use the complex when prepared and refrain from storing samples, especially near sources of heat or in sealed containers.

General experimental details were as previously described [2–4]. NMR spectra were obtained on the Nicolet 360 MHz instrument of the Atlantic Region Magnetic Resonance Centre, whose assistance is gratefully acknowledged. Spectra were run in either CDCl_3 or CD_2Cl_2 solution using either TMS, the CHCl_3 singlet at 7.26 or the CH_2Cl_2 triplet at 5.32 ppm as internal references. Elemental analyses were performed by the Canadian Microanalytical Service and molecular weight determinations by Galbraith Laboratories. $\text{Na}^{15}\text{NO}_2$ was obtained from MSD Isotopes and used as received. $\text{ReOCl}_3(\text{PPh}_3)_2$ was prepared by a previously published route [8] and $\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2$ was prepared using a modification of the method originally described by Chatt [9] (below).

Preparation of *mer-ReCl(CO)₃(PPh₃)₂*

$\text{ReOCl}_3(\text{PPh}_3)_2$ (2.00 g, 2.4 mmol) and PPh_3 (2.00 g, 7.6 mmol) were suspended in 70 ml of dichloromethane and subjected to 60 psi of carbon monoxide in a Fischer–Porter pressure bottle. The suspension was then heated to 80–100 °C for 45 min. After cooling and venting, 25 ml of ethanol was added to the resultant clear yellow solution and the dichloromethane removed under reduced pressure. The solid was then collected and recrystallized from dichloromethane and methanol (made slightly basic by the addition of a small amount of KOH) to give pale yellow plates (1.4 to 1.6 g, 70–80%).

Preparation of [Re(CH₃CN)₂(CO)₂(PPh₃)₂]ClO₄ (1)

mer-ReCl(CO)₃(PPh₃)₂ (1.00 g, 1.2 mmol) and AgClO₄ (0.37 g, 1.8 mmol) were heated under reflux in acetonitrile (100 ml) for 1 h, giving a clear colourless solution and a precipitate of AgCl. After cooling, the solution was filtered through a pad of Celite and the volume reduced to 5 mL under reduced pressure (CAUTION: Do not evaporate solutions containing perchlorate salts to dryness, an explosion could result). The white suspension was dissolved in 50 ml of dichloromethane and the solution treated with activated charcoal. Filtration resulted in a clear colourless solution which yielded a white crystalline solid following the addition of 30 ml of ethanol and evaporation of the dichloromethane under reduced pressure. Recrystallization was from dichloromethane/ethanol (1.13 g, 99%). M.p. 149 °C with explosive decomposition. Anal. Found: C, 53.23; H, 3.87; Cl, 3.71; N, 2.92. C₄₂H₃₆ClN₂O₆P₂Re calcd.: C, 53.19; H, 3.83; Cl, 3.74; N, 2.95%.

Reaction of [Re(CH₃CN)₂(CO)₂(PPh₃)₂]ClO₄ with NaNO₂. Preparation of Re(O, O'-NO₂)(CO)₂(PPh₃)₂ (2)

[Re(CH₃CN)₂(CO)₂(PPh₃)₂]ClO₄ (0.50 g, 0.53 mmol) and solid NaNO₂ (0.10 g, 1.4 mmol) were suspended in ethanol (30 ml) and heated under reflux for 30 min, after which time the suspension had turned bright yellow. The product was removed by filtration and recrystallized from dichloromethane/ethanol in the form of fine yellow crystals (0.39 g, 91%). M.p. 209 °C dec. Anal. Found: C, 55.62; H, 3.64; N, 1.72; P, 6.64; Mol. Wt, 735. C₃₈H₃₀NO₄P₂Re calcd.: C, 56.15; H, 3.72; N, 1.72; P, 7.62%; Mol. Wt, 813 (dichloromethane).

Reactions of Re(O, O'-NO₂)(CO)₂(PPh₃)₂

A. With CO. Preparation of Re(NO₂)(CO)₃(PPh₃)₂ (mixture of O- and N-bound isomers) (3). Re(O, O'-NO₂)(CO)₂(PPh₃)₂ (0.25 g, 0.31 mmol) was dissolved in 50 ml of dichloromethane and CO bubbled through the yellow solution for 15 min. The pale yellow solution was then diluted with 20 ml of ethanol and the dichloromethane removed under reduced pressure to yield a cream solid. Recrystallization was from dichloromethane/ethanol (0.26 g, 100%). M.p. dec. > 160 °C. Anal. Found: C, 55.52; H, 3.63; N, 1.64; P, 7.24. C₃₉H₃₀NO₅P₂Re calcd.: C, 55.71; H, 3.60; N, 1.67; P, 7.37%.

B. With p-tolylisocyanide (tic). Preparation of Re(NO₂)(CO)₂(tic)(PPh₃)₂ (mixture of O- and N-bound isomers) (4). Re(O, O'-NO₂)(CO)₂(PPh₃)₂ (0.20 g, 0.25 mmol) was dissolved in 20 ml of dichloromethane and to this solution was added 3.2 ml of a solution of tic in dichloromethane (10.0 mg ml⁻¹, 0.27 mmol). The solution lightened immediately and was allowed to stir for a further 30 min. The product was isolated by adding 15 ml of ethanol followed by evaporation under reduced pressure and recrystallized as above to give cream crystals (0.22 g, 96%). M.p. 184–186 °C dec. Anal. Found: C, 58.82; H, 4.01; N, 2.98. C₄₆H₃₇N₂O₄P₂Re calcd.: C, 59.41; H, 4.01; N, 3.01%.

C. With HCl. Re(O, O'-NO₂)(CO)₂(PPh₃)₂ (0.10 g, 0.12 mmol) was dissolved in 20 ml of dichloromethane. To this solution was added ethanolic HCl (2–3 drops of conc. HCl in 5 ml). The solution was stirred for 5 minutes, a further 10 ml of ethanol added and the volume reduced by evaporation. The white solid was collected by filtration and washed with ethanol and hexane (0.08 g, 75%). Infrared spectroscopy showed the product to consist of a mixture of *mer*-ReCl(CO)₃(PPh₃)₂

and $\text{ReCl}_2(\text{CO})(\text{PPh}_3)_2$ in roughly equivalent proportions [*mer*- $\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2$, $\nu(\text{CO})$ 2052w, 1958vs, 1914s cm^{-1} ; $\text{ReCl}_2(\text{CO})(\text{NO})(\text{PPh}_3)_2$, $\nu(\text{CO})$ 2012s cm^{-1} , $\nu(\text{NO})$ 1743s cm^{-1} (all in CH_2Cl_2 solution)].

Table 1

Spectroscopic data ^a

No.	Compound	$\nu(\text{CO})$ ^b	Others	NMR ^c
1	$[\text{Re}(\text{CH}_3\text{CN})_2(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$	1995, 1880		$\delta(^1\text{H})$; 1.64, t, CH_3CN $^2J(\text{HP})$ ca. 1 Hz 7.48, m, Ph
2	$\text{Re}(O, O'-\text{NO}_2)(\text{CO})_2(\text{PPh}_3)_2$	1939, 1864	ν_s ; 1241vw ν_{as} ; 1180s δ ; 887w	
	$\text{Re}(O, O'-^{15}\text{NO}_2)(\text{CO})_2(\text{PPh}_3)_2$		ν_s ; 1233vw ν_{as} ; 1152s δ ; 881w	
3	$\text{Re}(\text{NO}_2)(\text{CO})_3(\text{PPh}_3)_2$	2049mw, 2041m	NO_2 ; 1351s, 1317m, 632m	
	$\text{Re}(^{15}\text{NO}_2)(\text{CO})_3(\text{PPh}_3)_2$	1950, 1926, 1907	ONO ; 1416m, 1067s NO_2 ; 1323s, 1295m, 628m ONO ; 1391s, 1050s	
4	$\text{Re}(\text{NO}_2)(\text{C}_7\text{H}_7\text{NC})(\text{CO})_2(\text{PPh}_3)_2$	1967, 1898, 1878sh	NO_2 ; 1342s, 1314m, 629m ONO ; 1413w, 1070 w $\nu(\text{CN})$; 2136s	$\delta(^1\text{H})$ (nitro isomer); 2.32, s, CH_3 6.79, q, C_6H_4 , J_{AB} 8.3 Hz $\delta(^1\text{H})$ (nitrito isomer); 2.31, s, CH_3 6.61, q, C_6H_4 , J_{AB} 8.2 Hz
	$\text{Re}(^{15}\text{NO}_2)(\text{C}_7\text{H}_7\text{NC})(\text{CO})_2(\text{PPh}_3)_2$		NO_2 ; 1314s, 1288m, 625m ONO ; 1388w, 1054w	
	$\text{ReH}(\text{CO})_2(\text{PPh}_3)_3$ ^d	1930, <i>trans</i> to PPh_3 1868, <i>trans</i> to H	$\nu(\text{ReH})$; obscured	$\delta(^1\text{H})$ - 3.08, dt, $^2J(\text{HP}(1))$ 21.2 Hz $^2J(\text{HP}(2)) = ^2J(\text{HP}(3))$ 28.8 Hz $\delta(^{31}\text{P})$ 17.76, t, P(1); 25.12, d, P(2,3) $^2J(\text{P}(1)\text{P}(2,3))$ 22.1 Hz
	$\text{ReD}(\text{CO})_2(\text{PPh}_3)_3$ ^d	1929, <i>trans</i> to PPh_3 1855, <i>trans</i> to D	$\nu(\text{ReD})$; 1272w	$\delta(^{31}\text{P})$ 17.81, t, P(1); 25.11, d, P(2,3) $^2J(\text{P}(1)\text{P}(2,3))$ 22.1 Hz

^a Infrared spectra run as Nujol mulls unless indicated otherwise. Values in cm^{-1} . ^b All absorptions very strong unless otherwise indicated. ^c See experimental section. All signals gave satisfactory integrals.

^d Infrared data in dichloromethane solution.

D. With NaBH₄ and PPh₃. Preparation of mer-ReH(CO)₂(PPh₃)₃. Re(*O,O'*-NO₂)(CO)₂(PPh₃)₂ (0.25 g, 0.31 mmol), NaBH₄ (0.05 g, 1.3 mmol) and PPh₃ (0.15 g, 0.57 mmol) were suspended in 30 ml of ethanol and heated under reflux for 30 min. The cream product was removed by filtration, dissolved in dichloromethane and the solution filtered through a small pad of Celite. Following the addition of an equal volume of ethanol, evaporation of the solution yielded a cream crystalline solid (0.31 g, 98%). Characterization was by comparison with an authentic sample [10] and NMR spectroscopy (see Table 1). Utilizing NaBD₄ in the above procedure enabled the isolation of *mer*-ReD(CO)₂(PPh₃)₃.

Results and discussion

Our strategy in this project was to first prepare Re(NO₂)(CO)₃(PPh₃)₂ and examine its utility as a nitrosyl precursor, and then to generalize by developing routes to Re(NO₂)L(CO)₂(PPh₃)₂, the synthesis of which clearly requires a *d*⁶ rhenium precursor with two labile sites for the introduction of the L and NO₂⁻ ligands. Our initial efforts to generate Re(NO₂)(CO)₃(PPh₃)₂ from ReCl(CO)₃(PPh₃)₂ and AgNO₂ or [Re(CO)₄(PPh₃)₂]⁺ [11] with NO₂⁻ in the presence of Me₃NO were essentially successful save for the fact that the product was always contaminated with significant quantities of a dicarbonyl byproduct. We sought to overcome this difficulty by preparing [Re(CH₃CN)(CO)₃(PPh₃)₂]⁺ to react with the nitrite ion.

To our surprise, when *mer*-ReCl(CO)₃(PPh₃)₂ was allowed to react with AgClO₄ in refluxing acetonitrile, the product proved instead to be *cis-cis-trans*-[Re(CH₃CN)₂(CO)₂(PPh₃)₂]⁺ (**1**) (*trans* phosphines), which seemed ideally suited for the preparation of the general series of nitrite complexes above, not to mention numerous other complexes. The formation of the *bis*-acetonitrile derivative in this reaction undoubtedly results from the presence of *trans* carbonyls in the precursor, since a similar reaction employing *fac*-ReCl(CO)₃L₂ (L = 1,10-phen, 2,2'-biquinoline) yields [Re(CH₃CN)(CO)₃L₂]⁺ as the only product [11]. The stereochemistry of **1** is determined unequivocally by the observation of two equally intense ν (CO) absorptions in the infrared spectrum and, in the ¹H NMR, a single resonance for the acetonitrile protons which appears as a triplet due to coupling with two equivalent phosphorus nuclei. Spectroscopic data for all compounds are summarized in Table 1.

Treating **1** with NaNO₂ in ethanol suspension under reflux results in the rapid formation of a bright yellow crystalline precipitate which we have identified as the title complex, Re(*O,O'*-NO₂)(CO)₂(PPh₃)₂ (**2**). The infrared spectrum of compound **2** verifies it as the dicarbonyl byproduct formed in the various attempts to make Re(NO₂)(CO)₃(PPh₃)₂.

Only one band, at 1180 cm⁻¹, in the IR spectrum of **2** is readily identifiable as arising from the coordinated nitrite group. Comparing the spectrum of **2** with that of Re(*O,O'*-¹⁵NO₂)(CO)₂(PPh₃)₂, made in the same manner from Na¹⁵NO₂, however, reveals a total of three absorptions which shift on introduction of the label, the other two being at 1241vw and 887vw cm⁻¹. Of the numerous known forms of nitrite ligation [13], only that involving *O,O'*-chelation is consistent with these data. For example, [Ni(*O,O'*-NO₂)(*N,N'*-dimethylethylenediamine)]ClO₄ exhibits absorptions at 1215 vs (ν_{as}), 1295mw (ν_s) and 859mw (δ (NO₂)) [14]. In general,

coordination of the nitrite ligand in a symmetrical chelating fashion results in little change in the energy difference between ν_{as} and ν_{s} from that observed in the free ion (85 cm^{-1}) as well as an increase in the $\delta(\text{NO}_2)$ frequency [13]. Furthermore, it is to be expected that, as the coordination mode becomes less symmetrical, the energy gap between the two vibrations should increase and approach that of the nitrito ligand, typically in excess of 200 cm^{-1} . The energy gap between the symmetric and asymmetric modes in **2** of only 65 cm^{-1} , therefore, clearly establishes the nitrite ligand as being bound in a symmetric, chelating fashion. To the best of our knowledge, this mode of nitrite coordination in a low oxidation state organometallic complex is unknown and, for this reason, we have attempted at length to grow single crystals of **2** suitable for X-ray crystallography. All of our efforts to date, however, have yielded only dendritic crystals unsuitable for analysis.

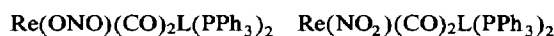
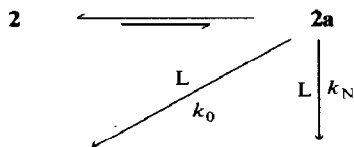
As expected, opening the chelate ligand in **2** proved to be facile. Thus, bubbling CO through a solution of **2** in dichloromethane resulted in rapid colour loss and the formation of **3**, as a mixture of *mer*- $\text{Re}(\text{NO}_2)(\text{CO})_3(\text{PPh}_3)_2$ and *mer*- $\text{Re}(\text{ONO})(\text{CO})_3(\text{PPh}_3)_2$ in approximately equal proportions. The ratio of these isomers is not affected noticeably by a change in temperature. Thus reacting **2** with CO at -23°C in dichloromethane and isolating the solid product at the same temperature results in no apparent change in the isomer ratio. Similarly, treating **2** with CO at 20 psi and 70°C for 14 h gave a product with an IR spectrum indistinguishable from those of **3** prepared rapidly at the lower temperatures. In similar fashion, **2** reacted with *p*-tolylisocyanide (tic) to give **4**, a mixture of *cis*- $\text{Re}(\text{NO}_2)(\text{CO})_2(\text{tic})(\text{PPh}_3)_2$ and *cis*- $\text{Re}(\text{ONO})(\text{CO})_2(\text{tic})(\text{PPh}_3)_2$, although in this case the ^1H NMR spectrum shows the N-bound to O-bound isomer ratio to be about 2/1. Examining the IR spectra of ^{15}N labelled **3** and **4** has enabled the assignment of nearly every nitrite absorption in these mixtures. In both cases, the values and energy separations of the ν_{as} and ν_{s} absorptions are typical of their respective coordination modes [13].

Heating mixture **3** under reflux in either dichloromethane/ethanol solution or ethanol suspension effects a gradual reversion to **2**. For example, the reversal is only about 20–30% complete after 1.5 h at 40°C and around 70–80% after 2 h refluxing in ethanol suspension. These observations in themselves are not out of the ordinary, since it is to be expected that the rate of CO elimination will be slower than the rate of addition. What is unusual, however, is the fact that the formation of **2** occurs almost entirely at the expense of the O-bound isomer, $\text{Re}(\text{ONO})(\text{CO})_3(\text{PPh}_3)_2$. Thus, after 1.5 h in refluxing dichloromethane/ethanol, the rate of O- to N-bound isomers in the residual **3** had dropped to about 1/2, and after 2 h in boiling ethanol, the residual **3** was present entirely as $\text{Re}(\text{NO}_2)(\text{CO})_3(\text{PPh}_3)_2$. In fact, under these conditions, it took close to 24 h for the last traces of the N-bound form of **3** to react.

The formation of **3** as a mixture of O- and N-bound isomers can be considered to occur in either of two ways; (i) one isomer is formed first and then rapidly isomerizes (thermodynamic control) or, (ii) the two isomers are formed directly from a common precursor and do not rapidly interconvert (kinetic control). The formation of mixture **3** directly from **2** under thermodynamic control is ruled out by the decarbonylation results, since facile nitro to nitrito interconversion would require a 1/1 isomer ratio to be maintained throughout the decarbonylation reaction. We are forced to conclude, therefore, that the two isomers present in **3** arise from the carbonylation of a common precursor via independent pathways. It seems self

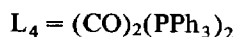
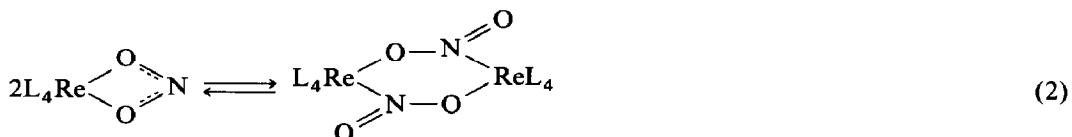
evident that this species cannot be **2**, since substitution at either Re–O bond would yield only the nitrito isomer, thereby implying that a compound possessing both Re–O and Re–N bonds is involved.

The simplest manner in which two pathways could exist for the addition reactions leading to **3** and **4**, would be for **2** to be in a rapid equilibrium with a second form, **2a**, present in solution in undetectable quantities. Under these circumstances, the ratios of the rate constants k_N and k_O would determine isomer ratios observed for **3** and **4**, viz;



Scheme 2

Clearly, the identity of the species **2a** is subject to speculation. We feel, however, that the nature of the putative equilibrium is probably best represented by one of the following two equations.



In both equilibria, the hypothetical second form of **2** results from a one-ended dissociation of the chelating nitrite ligand. In the first case, rotation around the Re–O bond followed by coordination of the nitrogen generates a second chelate complex. Nitrite coordination in this fashion has no precedent, although there are superficial similarities with other well known ligands such as bidentate acyls [15] and certain π -bond heterocumulenes such as CS_2 , RNCS and the like [16]. What does seem certain, however, is that the presence of the three-membered ring would make substitution very facile. In the second case, after one-ended dissociation, dimerization of the five-coordinate nitrito complex through nitrogen could generate a second form of **2** having *O,N*-bridging nitrite ligands. This mode of coordination has precedent [13], and Re–O bond cleavage in the dimer would result in formation of N-bound nitro complexes, and vice versa.

Some support for eq. 2 above is afforded by the reaction of **2** with coordinating acids such as HCl , which yields a mixture of $\text{ReCl(CO)}_3(\text{PPh}_3)_2$ and $\text{ReCl}_2(\text{NO})(\text{CO})(\text{PPh}_3)_2$. The formation of a nitrosyl once again suggests the existence of a Re–N interaction, and the facile and efficient transfer of a carbonyl group (assuming, as seems most likely, that it originates from the parent complex) would appear

to support the existence of a dimeric intermediate, somewhere along the reaction pathway.

Earlier in this paper we alluded to the potential synthetic utility of the bis(acetonitrile) complex **1**. We have as yet to fully explore this area but can at this stage report that treatment of **1** with PPh_3 and NaBH_4 in ethanol suspension gives reasonable yields of $\text{ReH}(\text{CO})_2(\text{PPh}_3)_3$. The published synthesis of this compound involves treatment of $\text{ReH}_5(\text{PPh}_3)_3$ with CO and stopping the reaction before significant quantities of $\text{ReH}(\text{CO})_3(\text{PPh}_3)_2$ form [10]. In our hands, this reaction has always proven difficult to control and has given only mediocre yields. Although the preparation of $\text{ReH}(\text{CO})_2(\text{PPh}_3)_3$ from **1** solves the problem of product purity, the yield of 65% is still unsatisfactory. This problem is nicely overcome by using the nitrite complex **2** instead, which increases the yield to 98%, resulting in an overall yield of 88% from $\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2$. Furthermore, this technique allows isolation of $\text{ReD}(\text{CO})_2(\text{PPh}_3)_3$ which, through the observation of a Fermi resonance interaction, enabled an assignment to be made of the carbonyl stretching frequencies (see Table 1).

Acknowledgements

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