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Synthesis and oxidation of chiral rhenium phosphine methyl complexes of the formula (η^5-C_5Me_5)Re(NO)(PR_3)(CH_3): in search of radical cations with enhanced kinetic stabilities

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Abstract

Reactions of racemic [(η^5-C_5Me_5)Re(NO)($NCCH_3$)(CO)]$^+$ BF_4^- and phosphines PR_3 (R = C_6H_5 **a**; 4-$C_6H_4CH_3$ **b**; 4-C_6H_4-*t*-C_4H_9 **c**; 4-$C_6H_4C_6H_5$ **d**; 4-$C_6H_4OCH_3$ **e**; *c*-C_6H_{11} **f**) give the phosphine carbonyl complexes [(η^5-C_5Me_5)Re(NO)(PR_3)(CO)]$^+$ BF_4^- (**5a**–**5f**$^+$ BF_4^-; 55–95%). These are treated with $LiEt_3BH$ and then BH_3·THF to give the phosphine methyl complexes (η^5-C_5Me_5)Re(NO)(PR_3)(CH_3) (**2a**–**2f**, 50–86%). Cyclic voltammetry shows that the new compounds **2b**–**2f** undergo chemically reversible one-electron oxidations that are thermodynamically more favorable than that of **2a** ($\Delta E° = 0.07, 0.07, 0.01, 0.09, 0.22$ V; CH_2Cl_2). The radical cations $\mathbf{2}^{\bullet+}$ X^- can be generated with Ag^+ X^- or (η^5-C_5H_5)$_2$Fe$^{\bullet+}$ X^- ($X^- = PF_6^-$, SbF_6^-), as evidenced by IR and ESR spectra, but are labile and efforts to isolate pure salts fail. Reaction of **2a** and TCNE give (η^5-C_5Me_5)Re(NO)(η^2-TCNE)(CH_3), which is crystallographically characterized and proposed to form by initial electron transfer followed by radical chain substitution. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Rhenium; Radical cations; Cyclic voltammetry; ESR; TCNE

1. Introduction

There is intense interest, from both fundamental and applied standpoints, in compounds where elemental sp carbon chains span two transition metals [1]. Our own studies have emphasized complexes in which at least one endgroup is the chiral rhenium fragment (η^5-C_5Me_5)Re(NO)(P(C_6H_5)$_3$) (**I**), which carries 17 valence electrons as a neutral entity [2–4]. Species with polyynediyl chains, –(C≡C)$_n$–, of up to 20 carbons can be isolated [2b]. In the case of dirhenium C_4 complexes [(η^5-C_5Me_5)Re(NO)(P(C_6H_5)$_3$)(CCCC)((C_6H_5)$_3$P)(ON)-Re(η^5-C_5Me_5)]$^{n+}$ $n$$PF_6^-$ ($\mathbf{1}^{n+}$ nPF_6^-), the radical cation $\mathbf{1}^{\bullet+}$ PF_6^- and dication $\mathbf{1}^{2+}$ $2PF_6^-$ can also be synthesized and isolated [2a]. These compounds, which are illustrated in Scheme 1, exhibit a variety of fascinating structural and electronic properties. However, the C_6 and C_8 homologs are dramatically less stable. Similar trends have been described by Lapinte with iron endgroups [5,6]. Nonetheless, he was able to isolate the C_8 radical cation [(η^5-C_5Me_5)Fe(dppe)(CCCCCCCC)-(dppe)Fe(η^5-C_5Me_5)]$^{\bullet+}$ PF_6^- in analytically pure form [5b]. This synthetic triumph has never been equaled.

Accordingly, we have sought analogs of the endgroup **I** that would give more stable oxidation products. One obvious approach would be to utilize phosphines that are more electron releasing than triphenylphosphine. This should lead to thermodynamically more favorable oxidations and $E°$ values. From linear free energy considerations, the rates of several possible types of decomposition reactions (e.g. atom abstraction, dimerization) would likely be retarded. Another approach would involve bulkier phosphines, which should sterically inhibit all types of bimolecular reactions. Alternatively, replacement of the nitrosyl lig-

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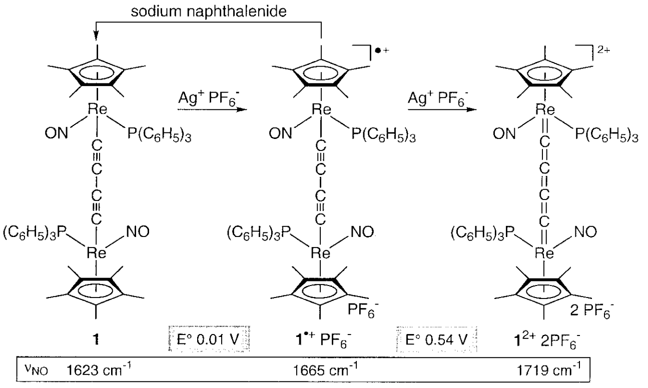


Scheme 1. Interconversion of the dirhenium C_4 complexes $\mathbf{1}^{n+}$ $n\mathrm{PF}_6^-$.

and, which is a good π acceptor, by a more basic ligand should help. However, a three-electron donor would be required, a somewhat less flexible or tunable ligand class. This overall strategy can best be implemented by substituting a two-electron donor ligand, and simultaneously changing to a metal with an additional valence electron. In this way one arrives at the iron cyclopentadienyl bis(phosphine) endgroups of Lapinte [5] and related ruthenium systems of Bruce [6].

We set out to build the necessary foundation for preparing C_6 and C_8 analogs of $\mathbf{1}^{n+}$ $n\mathrm{X}^-$ with more electron releasing and bulkier phosphines. The first objective was to synthesize methyl complexes of the formula $(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(CH_3)$ (**2**). The parent triphenylphosphine compound $(\eta^5\text{-}C_5Me_5)Re(NO)(P(C_6H_5)_3)(CH_3)$ (**2a**) [7] is a key precursor to all higher polyynediyl homologs of **1** [2,3]. The second objective was to characterize the oxidation potentials of **2**, and conduct exploratory preparative reactions. We noted earlier that cyclic voltammograms of **2a** show chemically reversible one-electron oxidations [3a]. However, attempts to isolate radical cations $\mathbf{2a}^{\bullet+}$ X^- have to date failed. Improved kinetic stabilities with any of the new phosphine ligands would likely be mirrored in the corresponding C_6 and C_8 dirhenium radical cations.

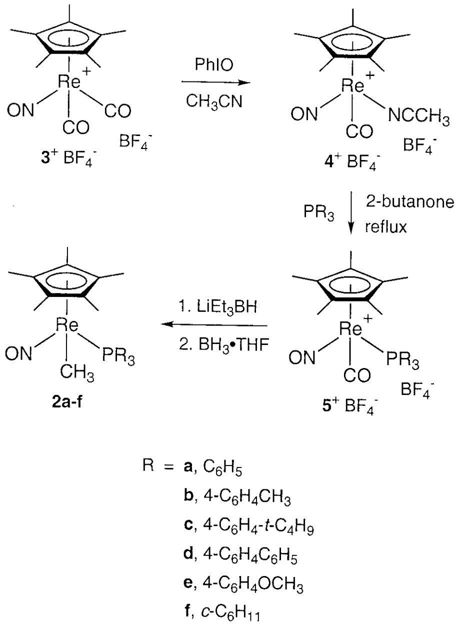
In this paper, we report syntheses of five new complexes of the formula **2**, each featuring a readily available phosphine that is a stronger donor and/or bulkier than triphenylphosphine. Their oxidation potentials and reactions that give labile radical cations $\mathbf{2}^{\bullet+}$ X^- are described. In the following paper [8], we report the isolation and crystal structure of one such radical cation, and diverse supporting experiments that help to interpret its physical and chemical properties. In future papers [9], we will detail analogous complexes of new, heretofore unprecedented classes of phosphines, and their successful applications to the carbon chain complex chemistry outlined above.

2. Results

2.1. Syntheses of phosphine complexes

The previously reported preparation of triphenylphosphine complex **2a** is shown in Scheme 2 [7]. Analogous procedures were found to work well for other phosphines. First, the readily available cationic dicarbonyl complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(CO)_2]^+$ BF_4^- ($\mathbf{3}^+$ BF_4^-) [7] was combined with iodosobenzene in acetonitrile to give the isolable monocarbonyl solvent complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(NCCH_3)(CO)]^+$ BF_4^- ($\mathbf{4}^+$ BF_4^-). This was subsequently treated, with or without purification, with 1–2 equivalents of the phosphines **b**–**f** (Scheme 2). The triarylphosphines **b**, **e**, which feature electron-releasing *p*-methyl or *p*-methoxy groups, are commercially available. The bulkier *p*-*t*-butyl homolog **c** is easily prepared [10], as is the *p*-phenyl system **d** [11]. The latter was selected more for size and possible crystallinity-enhancing characteristics than for electronic properties. Tri(cyclohexyl)phosphine **f** is commercially available, and distinctly more electron releasing than triphenylphosphine [12].

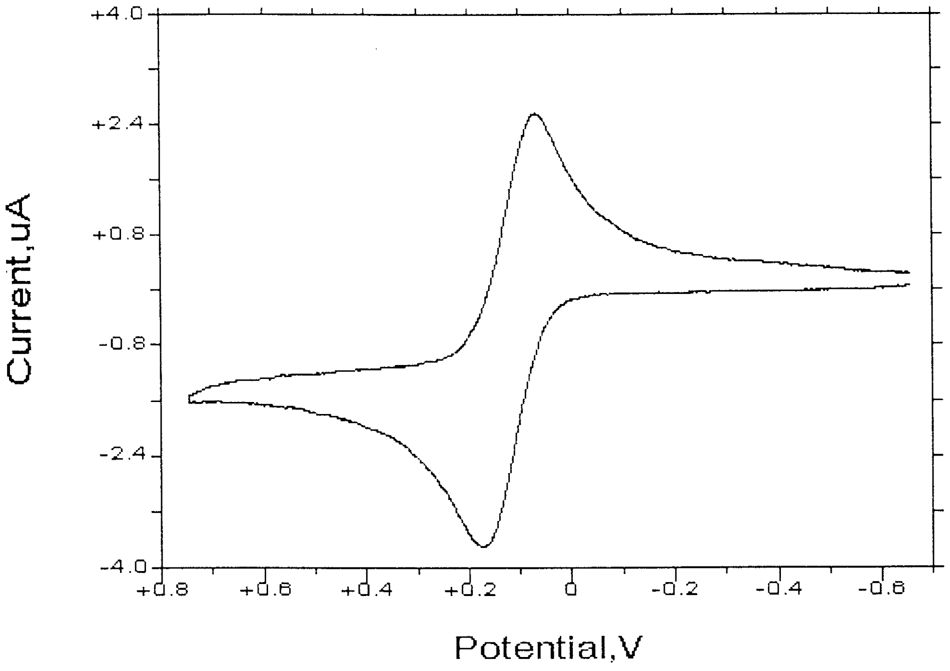
Workups gave the new carbonyl phosphine complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(CO)]^+$ BF_4^- (**5b**–$\mathbf{5f}^+$ BF_4^-) as air stable yellow powders. No attempts were made to optimize yields, which ranged from 95% to 55%. Complexes **5b**–$\mathbf{5f}^+$ BF_4^- were characterized by microanalysis, mass spectrometry, IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopies, as described in Section 4. In all cases, properties closely matched those of the triphenylphosphine complex $\mathbf{5a}^+$ BF_4^-. The ^{13}C-NMR



Scheme 2. Synthesis of rhenium phosphine complexes.

spectra showed doublets for the CO ligands at 209.9 to 201.0 ppm (J_{CP} = 7.9–8.5 Hz). The IR ν_{CO} and ν_{NO} data are summarized in Table 1. The tri(cyclohexyl)phosphine complex **5f**$^+$ BF_4^- gave slightly lower values, indicating enhanced backbonding to the carbonyl and nitrosyl ligands, consistent with the high phosphine basicity. The tri(*p*-(phenyl)phenyl)phosphine complex **5d**$^+$ BF_4^- gave slightly higher values. The others gave values that were identical within experimental error.

Complexes **5b**–**5f**$^+$ BF_4^- were treated with $LiEt_3BH$ and then BH_3·THF (Scheme 2). This two-step reduction, which involves an intermediate formyl complex [7], gave the target methyl phosphine complexes (η^5-C_5Me_5)Re(NO)(PR_3)(CH_3) (**2b**–**2f**) in 50–86% unoptimized yields. The one-step $NaBH_4$ reduction used in the cyclopentadienyl series [13] afforded poorer yields. Complexes **2b**–**2f** were air sensitive red powders or crystals that were stored under nitrogen. Their benchtop stabilities were noticeably greater in the arid Salt Lake City climate than the humid Erlangen, Germany climate. They were characterized analogously to **5b**–**5f**$^+$ BF_4^-, and properties closely matched those of **2a**. The ^{13}C-NMR spectra of **2b**–**2f** showed doublets for the methyl ligands at −21.6 to −27.3 ppm (J_{CP} = 6.6–8.7 Hz). The IR ν_{NO} values (Table 1) showed a greater spread than with **5b**–**5f**$^+$ BF_4^-. Analogous sequences were conducted with PMe_3 and $P(CH_2CH_2\text{-}n\text{-}C_6F_{11})_3$



Complex	$E_{p,a}$ [V]	$E_{p,c}$ [V]	E° [V]	ΔE [mV]	$i_{c/a}$
2a	0.22	0.15	0.19	70	1
2b	0.17	0.06	0.12	110	1
2c	0.18	0.08	0.12	100	1
2d	0.24	0.12	0.18	120	1
2e	0.14	0.06	0.10	80	1
2f	0.01	-0.07	-0.03	80	1

(a) 1-3 × 10^{-3} M in 0.1 M Bu_4N^+ BF_4^-/CH_2Cl_2 at 22.5 ± 1 °C; Pt working and counter electrodes, potential vs Ag wire pseudoreference; scan rate 100 mV/s; ferrocene = 0.46 V.

Chart 1. Cyclic voltammetry data for methyl complexes **2a**–**f**.

Table 1
Key IR data (cm^{-1}, CH_2Cl_2)

Complex	ν_{NO}	ν_{CO}
5a$^+$ BF_4^-	1741	2002
5b$^+$ BF_4^-	1743	2002
5c$^+$ BF_4^-	1743	2002
5d$^+$ BF_4^-	1745	2006
5e$^+$ BF_4^-	1742	2001
5f$^+$ BF_4^-	1737	1993
2a	1606	
2b	1603	
2c	1601	
2d	1606	
2e	1594	
2f	1599	

[14]. Data on these carbonyl and methyl complexes, which did not advance the objectives of this study and were only partially characterized, are presented elsewhere [15].

2.2. Oxidations

Cyclic voltammograms of **2b**–**2f** were recorded in CH_2Cl_2. The conditions and data are summarized in Chart 1 [16] which contains a representative trace. All complexes exhibited chemically reversible one-electron oxidations, presumably representing radical cations $\mathbf{2}^{\bullet+}$ X^-, and no further reversible oxidations at potentials as high as 1.2 V. All were thermodynamically easier to oxidize than **2a**. The $E°$ values tracked the IR ν_{NO} values, except for a reversal with the tri(*p*-methoxyphenyl)phosphine and tri(cyclohexyl)phosphine complexes **2e** and **2f**. The latter was the easiest to oxidize, comparable to the dirhenium C_4 complex **1** (Scheme 1). The separations of the anodic and cathodic peaks varied from 70 to 120 mV, reflecting fine points and gradations of reversibilities that remain under investigation.

Preparative oxidations were investigated next. Both silver and ferrocenium cations are effective with **1** [2]. Accordingly, **2a**–**2d**, **2f** and Ag^+ PF_6^- (1 equivalent) or $(\eta^5\text{-}C_5H_5)_2Fe^{\bullet+}$ X^- ($X^- = PF_6^-$ or SbF_6^-; 1–1.5 equivalent)[17] were combined in CH_2Cl_2 as shown in Chart 2. In all cases, solutions darkened. IR monitoring showed shifts of the ν_{NO} bands from 1599–1606 to 1710–1720 cm^{-1}, consistent with the reduced back-bonding that would be expected in radical cations **2a**–**2d**, $\mathbf{2f}^{\bullet+}$ X^-. This is approximately twice the shift found upon generation of the mixed valence radical cation $\mathbf{1}^{\bullet+}$ PF_6^- (Scheme 1), in which the positive charge is delocalized between two rheniums. The products were stable for hours in solution at room temperature. Repeated efforts were made to isolate or crystallize these species. The PF_6^- salts were not stable in the solid state, but solid $\mathbf{2a}^{\bullet+}$ SbF_6^- was stable for 5–15 min under nitrogen.

Additional evidence for the formation of $\mathbf{2}^{\bullet+}$ X^- was sought. Thus, representative ESR spectra were recorded, as illustrated in Chart 2. Sextets were observed, similar to a spectrum of $\mathbf{2a}^{\bullet+}$ PF_6^- reported earlier [3a]. The individual lines were broad, and the $A_{iso,Re}$ values ranged from 185 to 206 G (**a**, 197; **b**, 185; **c**, 198; **d**, 206; **f**, 193 G). The multiplicity follows from the 5/2 nuclear spin of the principle rhenium isotopes (^{185}Re, ^{187}Re), which have nearly identical magnetic

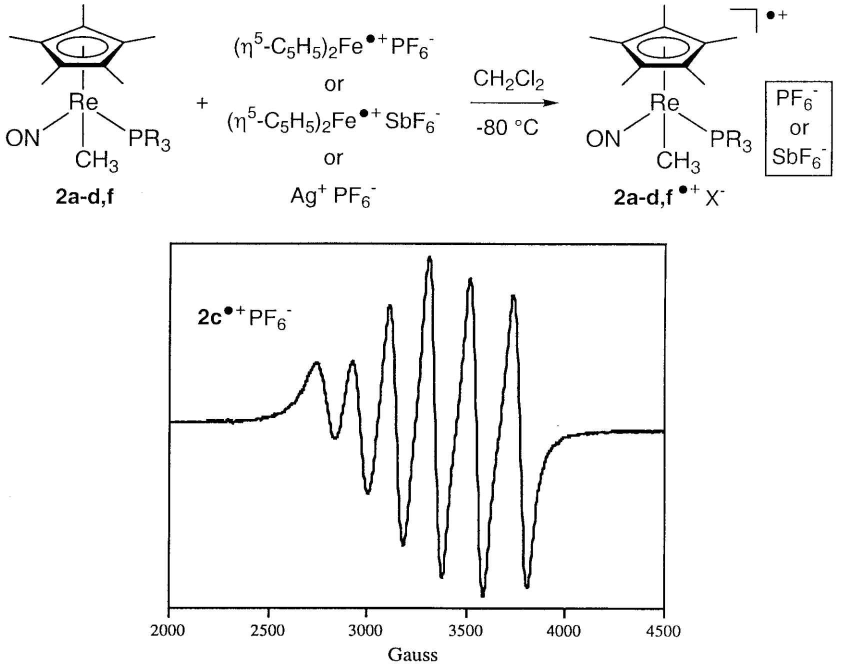
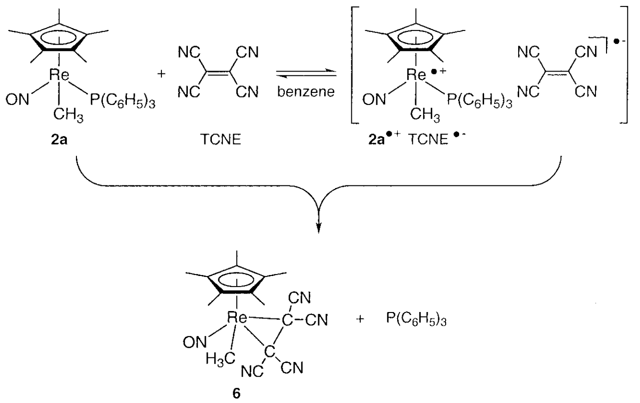


Chart 2.



Scheme 3. Reaction with TCNE.

moments. Importantly, the $A_{iso,Re}$ values are approximately twice that of the delocalized dirhenium radical cation **1**$^{\bullet+}$ PF_6^- (98 G). No other couplings have ever been resolved in this series of compounds. Two isomeric rhenium centered radicals of the formula $[Re(CO)_3(P(C{-}C_6H_{11})_3)_2]$ gave $A_{iso,Re}$ values of 190 and 156 G, respectively [18].

2.3. Reaction with TCNE

In the course of the exploratory oxidation chemistry described above, **2a** and TCNE were combined in benzene as shown in Scheme 3. TCNE is well known to serve as a one-electron oxidant. However, it is thermodynamically more difficult to reduce than $(\eta^5\text{-}C_5H_5)_2Fe^{\bullet+}$ X^-, with a difference of 270 mV in CH_3CN [16b]. Hence, it is a weaker oxidant, and the $E°$ data in Chart 1 indicate that it would not necessarily give complete conversion to **2a**$^{\bullet+}$ TCNE$^{\bullet-}$. Interestingly, an IR spectrum showed a rapid and quantitative reaction, with a much larger shift of the ν_{NO} band (1606 to 1753 cm^{-1}) than for the oxidations in Chart 2. A crystalline, diamagnetic product **6** was isolated in high yield. The ^1H and ^{13}C-NMR spectra showed methyl ligand signals that were no longer coupled to phosphorus. No ^{31}P-NMR signal could be detected. A strong IR band at 2234 cm^{-1} suggested the presence of cyano groups. Mass spectral and microanalytical data were consistent with the formulation $(\eta^5\text{-}C_5Me_5)Re(NO)(\eta^2\text{-TCNE})(CH_3)$ (**6**).

In order to establish unequivocally the identity of **6**, a crystal structure was determined as outlined in Table 2 and Section 4. Fig. 1 confirms the proposed formulation, and Table 3 lists key bond lengths and angles. Structural features and mechanistic implications are analyzed below.

Table 2
Crystallographic data for **6**

Molecular formula	$C_{17}H_{18}N_5ORe$
Fomula weight	494.57
Crystal dimensions (mm)	0.22 × 0.24 × 0.34
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	9.294(1)
b (Å)	13.728(1)
c (Å)	14.089(1)
β (°)	91.22(2)
V (Å^3)	1797.2(2)
Z	4
T (K)	296
D_{calc} (g cm^{-3})	1.828
D_{found} (g cm^{-3}) (CH_3I/CCl_4)	1.80
Absorption coefficient (cm^{-1})	67.78
F(000)	952
Diffractometer	MAR research image plate
Radiation (Å)	0.71073 (Mo–K$_\alpha$)
2θ Range (°)	2.0–51.3
Scan type	ω-rotation
No. of frames	65
Exposure per frame (min)	8
Detector distance (mm)	120
Index ranges (h, k, l)	0–11, 0–16, −17–17
Reflections collected	31488
Independent reflections	3336 (R_{int} = 0.038)
Observed reflections	2231 [$I > 3\sigma(I)$]
Weighting scheme	$w = 1/\sigma^2(F_o)$, $p = 0.002$
R, R_w [a]	0.036, 0.030
Goodness-of-fit	$S = 2.20$
Δ/σ (max)	0.01
Number of parameters	226
Δ/ρ (max) (e Å^{-3})	1.10

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$; $R_w = [\Sigma(w(|F_o| - |F_c|)^2/\Sigma(w|F_o|^2)]^{1/2}$.

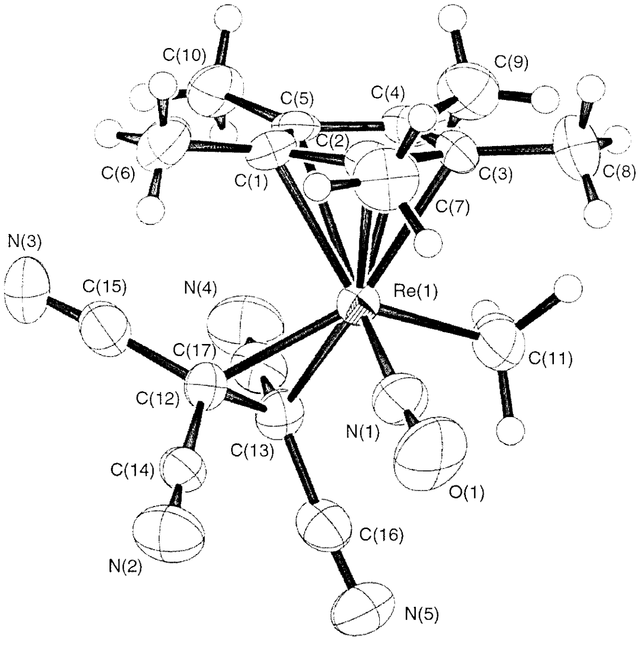


Fig. 1. Molecular structure of TCNE complex **6**.

3. Discussion

Chart 1 shows that the replacement of the triphenylphosphine ligand in **2a** by more electron-re

Table 3
Key bond lengths (Å) and angles (°) for **6**

Bond lengths			
Re(1)–N(1)	1.755(6)	Re(1)–C(1)	2.332(8)
Re(1)–C(2)	2.302(8)	Re(1)–C(3)	2.296(8)
Re(1)–C(4)	2.364(7)	Re(l)–C(5)	2.357(7)
Re(1)–C(11)	2.18(1)	Re(1)–C(12)	2.171(8)
Re(1)–C(13)	2.186(8)	O(1)–N(1)	1.174(7)
N(2)–C(14)	1.152(10)	N(3)–C(15)	1.116(9)
N(4)–C(17)	1.133(9)	N(5)–C(16)	1.133(10)
C(1)–C(2)	1.42(1)	C(1)–C(5)	1.44(1)
C(1)–C(6)	1.49(1)	C(2)–C(3)	1.43(1)
C(2)–C(7)	1.50(1)	C(3)–C(4)	1.448(10)
C(3)–C(8)	1.49(1)	C(4)–C(5)	1.40(1)
C(4)–C(9)	1.47(1)	C(5)–C(10)	1.541(9)
C(12)–C(13)	1.49(1)	C(12)–C(14)	1.44(1)
C(12)–C(15)	1.48(1)	C(13)–C(16)	1.46(1)
C(13)–C(17)	1.42(1)	Re(1)–C_5Me_5(centroid)	1.987
Bond angles			
N(1)–Re(1)–C(11)	91.2(4)	N(1)–Re(1)–C(13)	98.7(3)
N(1)–Re(1)–C(12)	91.7(3)	N(2)–C(14)–C(12)	176.4(10)
C(11)–Re(1)–C(12)	120.5(4)	C(11)–Re(1)–C(13)	81.0(4)
C(12)–Re(1)–C(13)	39.9(3)	Re(1)–C(12)–C(13)	70.6(5)
Re(1)–C(12)–C(14)	114.5(5)	Re(1)–C(12)–C(15)	122.7(6)
Re(1)–N(1)–O(1)	172.6(7)	N(3)–C(15)–C(12)	177(1)
N(4)–C(17)–C(13)	176(1)	N(5)–C(16)–C(13)	176.7(10)
C(13)–C(12)–C(14)	118.2(7)	C(13)–C(12)–C(15)	115.0(7)
C(14)–C(12)–C(15)	110.8(7)	Re(1)–C(13)–C(12)	69.5(5)
Re(1)–C(13)–C(16)	115.7(5)	Re(1)–C(13)–C(17)	114.0(6)
C(12)–C(13)–C(16)	118.5(7)	C(12)–C(13)–C(17)	118.3(7)
C(16)–C(13)–C(17)	113.6(8)		

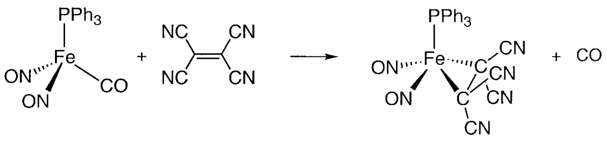
leasing triaryl- or trialkylphosphines can render oxidation up to 0.220 V thermodynamically more favorable. Interestingly, while this work was in progress an electrochemical study of related cyclopentadienyl iron acetyl complexes ($(\eta^5\text{-}C_5H_5)Fe(CO)(PR_3)(COMe)$) (**7**) was published [19]. The differences in $E°$ values between the triphenylphosphine complex **7a** and tri(*p*-methylphenyl)-, tri(*p*-methoxyphenyl)-, and tri(cyclohexyl)-phosphine complexes **7b**, **e**, **f** (CH_3CN, 20°C: 0.028, 0.044, 0.197 V) were similar to those between **5a** and **5b**, **e**, **f** (0.07, 0.09, 0.22 V). An analogous trend has been reported for the cobalt bis(phosphine) complexes $[Co(CNCMe_3)_3(PR_3)_2]^+\ ClO_4^-$ [20].

Although the radical cations $\mathbf{2}^{\bullet+}\ X^-$ are easily generated and spectroscopically characterized, the phosphine ligands investigated are not in themselves sufficient to render them easily isolable. In the absence of mechanistic studies, one can only speculate on the exact problem. For example, the less bulky and less electron-rich cyclopentadienyl radical $[(\eta^5\text{-}C_5H_5)Re(NO)(P(C_6H_5)_3)(CH_3)]^{\bullet+}\ PF_6^-$ undergoes a rapid second-order decomposition in acetonitrile ($\Delta H^{\ddagger} = 0.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -46$ eu) to give methane (0.5 equivalent), the methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(P(C_6H_5)_3)(=CH_2)]^+\ PF_6^-$ (0.5 equivalent), and the acetonitrile complex $[(\eta^5\text{-}C_5H_5)Re(NO)(P(C_6H_5)_3)(NCCH_3)]^+\ PF_6^-$ (0.5 equivalent) [21]. However, as detailed in the following paper [8], when the radical cations $\mathbf{2}^{\bullet+}$ are paired with appropriate bulky anions, dramatic stability enhancements can be achieved.

The reaction of **2a** and TCNE (Scheme 3) highlights yet another potential complication in the quest for isolable 17 valence electron organometallic compounds: their well documented substitution lability [22,23]. We are aware of one close literature precedent for the formation of TCNE complex **6**, the replacement of an iron carbonyl ligand shown in Scheme 4 [24]. These investigators proposed a radical chain mechanism, consistent with extensive studies by Kochi with $(\eta^5\text{-}C_5H_5)M(L)(L')(L'')$ complexes related to **2** [23]. The probable sequence of steps in both the iron and rhenium reactions is generalized at the bottom of Scheme 4.

Our TCNE complex belongs to a large class of compounds of the general formula $(\eta^5\text{-}C_5R_5)M(XO)(\eta^2\text{-}C{=}Y)(Z)$, the structural and electronic properties of which have been extensively analyzed [25]. Such complexes are formally octahedral, as evidenced by the 91.2(4)° ON–Re–CH_3 bond angle in **6**. The conformation of the TCNE ligand maximizes overlap of the C=C π^* acceptor orbital with the one rhenium d orbital that cannot backbond into the nitrosyl ligand. This lies in a plane perpendicular to the rhenium–nitrosyl bond. Accordingly, the plane defined by rhenium and the ligating TCNE carbons makes 7.8° and 101.6° angles with the Re–CH_3 and Re–NO bonds, respectively. Structures of TCNE complexes have also been extensively analyzed [26]. The $(NC)_2C{-}C(CN)_2$ bond length (1.49(1) Å) is consistent with a metallacyclopropane resonance form. Together with the IR ν_{CN} value of > 2200 cm^{-1}, this indicates a formal TCNE oxidation state of −II, and thus a formal rhenium oxidation state of +III.

In summary, this paper has described our 'first generation' approach to longer chain homologs of the C_4 dirhenium radical cation $\mathbf{1}^{\bullet+}\ X^-$ and dication $\mathbf{1}^{2+}\ 2X^-$ with improved stabilities. The relatively inauspicious



$$(1)\quad M(L) + TCNE \rightleftharpoons M(L)^{\bullet+}\,TCNE^{\bullet-}$$

$$(2)\quad M(L)^{\bullet+}\,TCNE^{\bullet-} + TCNE \rightleftharpoons M(TCNE)^{\bullet+}\,TCNE^{\bullet-} + L$$

$$(3)\quad M(TCNE)^{\bullet+}\,TCNE^{\bullet-} + M(L) \rightleftharpoons M(TCNE) + M(L)^{\bullet+}\,TCNE^{\bullet-}$$

$$(2{+}3)\ M(L) + TCNE \rightleftharpoons M(TCNE) + L$$

Scheme 4. Literature precedent for substitution by TCNE and probable mechanism.

beginnings with model compounds **2b**–**2f**$^{\bullet+}$ X^- are in fact mirrored in the corresponding C_6 and C_8 complexes [15]. However, from the standpoint of a strategic step in an ultimately successful quest [9], these data provide an instructive example of design and tactics in targeted organometallic synthesis.

4. Experimental

4.1. General data

General procedures and solvent purifications were identical to those in two recent papers [2b,27], and are further detailed elsewhere [15]. Reducing agents, TCNE, and phosphines for which no citations are provided were obtained from common commercial vendors and used without purification. Cyclic voltammetry was conducted as previously described [2]. ESR measurements utilized a Bruker ESP-300E spectrometer equipped with an ER 4116 DM dual mode X-band cavity and an Oxford Instruments ESR-900 helium flow cryostat. Spectra were recorded at a sweep rate of 100 G s^{-1} and a microwave frequency of 9.65 GHz (precise microwave frequencies were recorded for individual spectra to ensure precise *g*-alignment; modulation frequency and amplitude, 100 kHz and 12.6 G).

4.2. $[(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(CO)]^+$ BF_4^- (**5b**$^+$ BF_4^-)

A Schlenk flask was charged with CH_3CN (100 ml) and $[(\eta^5\text{-}C_5Me_5)Re(NO)(CO)_2]^+$ BF_4^- (**3**$^+$ BF_4^- [7]; 1.001 g, 2.020 mmol), and cooled to 0°C. Then iodosobenzene (0.450 g, 2.020 mmol) [28] was added with stirring. The cold bath was removed. The solution was kept 3 h at room temperature [29], and the solvent was removed by rotary evaporation. The dark oily residue was washed with Et_2O (2×50 ml). Then $P(4\text{-}C_6H_4CH_3)_3$ (1.220 g, 4.011 mmol) and 2-butanone (100 ml) were added. The mixture was refluxed. After 3 h, the solvent was removed by rotary evaporation. The gold solid was transferred to a fritted glass funnel, washed with hexane (10 ml) and Et_2O (3×20 ml), and dissolved in a minimum of acetone. The solution was layered with Et_2O, and stored at −20°C. After 2 days, a yellow powder was isolated by filtration, washed with Et_2O (10 ml), and air dried to give **5b**$^+$ BF_4^- (1.051 g, 1.360 mmol, 68%), m.p. 247–249°C [30]. ^1H-NMR ([D_6]acetone) [32]: $\delta = 7.47$ (br d, $J_{HH} = 6.6$ Hz, $3m$-C_6H_4), 7.34 (dd, $J_{HP} = 12.0$ Hz, $J_{HH} = 8.0$ Hz, $3o$-C_6H_4), 2.43 (s, $3ArCH_3$), 2.04 (s, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ $\delta = 209.9$ (d, $J_{CP} = 7.9$ Hz, CO), 143.7 (s, p-C_6H_4), 133.9 (d, $J_{CP} = 12.3$ Hz, o-C_6H_4), 131.0 (d, $J_{CP} = 12.1$ Hz, m-C_6H_4), 128.1 (d, $J_{CP} = 59.8$ Hz, i-C_6H_4), 107.2 (s, $C_5(CH_3)_5$), 21.4 (s, $ArCH_3$), 10.1 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ $\delta = 13.7$ (s). MS [31] 684 (**5b**$^+$). Anal. Calc. for $C_{32}H_{36}NO_2PReBF_4$: C 49.88, H 4.71. Found: C 49.62, H 4.80%.

4.3. $[(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4\text{-}t\text{-}C_4H_9)_3)(CO)]^+$ BF_4^- (**5c**$^+$ BF_4^-)

Reactions analogous to those for **5b**$^+$ BF_4^- were conducted with CH_3CN (60 ml), **3**$^+$ BF_4^- (0.427 g, 0.864 mmol), iodosobenzene (0.199 g, 0.907 mmol), $P(4\text{-}C_6H_4\text{-}t\text{-}C_4H_9)_3$ (0.548 g, 1.274 mmol) [10], and 2-butanone (60 ml). An identical workup gave **5c**$^+$ BF_4^- as a yellow powder (0.429 g, 0.478 mmol, 55%), m.p. 299–300°C dec. [30]. ^1H-NMR (CD_2Cl_2) [32]: $\delta = 7.57$ (dd, $J_{HP} = 2.4$ Hz, $J_{HH} = 8.4$ Hz, $3m$-C_6H_4), 7.32 (dd, $J_{HP} = 12.0$ Hz, $J_{HH} = 8.4$ Hz, $3o$-C_6H_4), 1.94 (s, $C_5(CH_3)_5$), 1.34 (s, $3ArC(CH_3)_3$). $^{13}C\{^1H\}$ $\delta = 201.6$ (d, $J_{CP} = 7.9$ Hz, CO), 156.6 (d, $J_{CP} = 2.1$ Hz, p-C_6H_4), 133.3 (d, $J_{CP} = 11.8$ Hz, o-C_6H_4), 127.4 (d, $J_{CP} = 60.2$ Hz, i-C_6H_4), 127.0 (d, $J_{CP} = 11.4$ Hz, m-C_6H_4), 106.6 (s, $C_5(CH_3)_5$), 35.5 (s, $ArC(CH_3)_3$), 31.3 (s, $ArC(CH_3)_3$), 10.2 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ $\delta = 12.0$ (s). MS [31] 810 (**5c**$^+$). Anal. Calc. for $C_{41}H_{54}BF_4NO_2PRe$: C 54.91, H 6.07. Found: C 54.79, H, 6.06%.

4.4. $[(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4C_6H_5)_3)(CO)]^+$ BF_4^- (**5d**$^+$ BF_4^-)

A Schlenk flask was charged with $[(\eta^5\text{-}C_5Me_5)Re(NO)(NCCH_3)(CO)]^+$ BF_4^- (**4**$^+$ BF_4^- [7]; 1.050 g, 2.070 mmol), $P(4\text{-}C_6H_4C_6H_5)_3$ (1.070 g, 2.181 mmol) [11], and 2-butanone (10 ml). The mixture was refluxed (3 h), and concentrated by rotary evaporation (ca. 3 ml). The solution was poured into rapidly stirred Et_2O (200 ml). The yellow precipitate was isolated by filtration and air dried to give **5d**$^+$ BF_4^- (1.870 g, 1.950 mmol, 95%), m.p. 268–270°C dec. [30]. ^1H-NMR (CD_2Cl_2) [32]: $\delta = 7.87$ (dd, $J_{HP} = 2.4$ Hz, $J_{HH} = 8.4$ Hz, $3m$-C_6H_4), 7.70 (br d, $J_{HH} = 8.0$ Hz, $3o$-C_6H_4), 7.6–7.4 (m, $3C_6H_5$) 2.04 (s, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ $\delta = 201.0$ (d, $J_{CP} = 8.2$ Hz, CO), 145.6 (d, $J_{CP} = 2.7$ Hz, p-C_6H_4), 139.3 (d, $J_{CP} = 1.1$ Hz, i-C_6H_5), 134.0 (d, $J_{CP} = 11.8$ Hz, o-C_6H_4), 129.6 (s, o-C_6H_5), 129.2 (s, p-C_6H_5), 129.0 (d, $J_{CP} = 59.0$ Hz, i-C_6H_4), 128.6 (d, $J_{CP} = 11.5$ Hz, m-C_6H_4), 127.7 (s, m-C_6H_5), 106.8 (br d, $J_{CP} = 0.8$ Hz, $C_5(CH_3)_5$), 10.4 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ $\delta = 13.4$ (s). MS [31] 870 (**5d**$^+$). Anal. Calc. for $C_{47}H_{42}BF_4NO_2PRe$: C 59.00, H 4.42. Found: C 58.93, H 4.51%.

4.5. $[(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4OCH_3)_3)(CO)]^+$ BF_4^- (**5e**$^+$ BF_4^-)

A reaction analogous to that for **5d**$^+$ BF_4^- was conducted with **4**$^+$ BF_4^- (0.426 g, 0.833 mmol), $P(4\text{-}C_6H_4OCH_3)_3$ (0.380 g, 1.08 mmol), and 2-butanone (20 ml). An identical workup gave **5e**$^+$ BF_4^- as a yellow powder (0.490 g, 0.598 mmol, 72%), m.p. 235–237°C dec. [30]. ^{1}H-NMR (CD_2Cl_2) [32]: $\delta = 7.26$ (dd, $J_{HP} = 12$ Hz, $J_{HH} = 9$ Hz, 3*o*-C_6H_4), 7.06 (dd, $J_{HP} = 1.8$ Hz, $J_{HH} = 9$ Hz, 3*m*-C_6H_4), 3.87 (s, 3OCH_3), 1.98 (s, $C_5(CH_3)_5$). $^{13}C\{^{1}H\}$ $\delta = 201.5$ (d, $J_{CP} = 8.5$ Hz, *C*O), 162.9 (s, *p*-C_6H_4), 134.9 (d, $J_{CP} = 13.1$ Hz, *o*-C_6H_4), 121.7 (d, $J_{CP} = 63.8$ Hz, *i*-C_6H_4), 115.4 (d, $J_{CP} = 12.0$ Hz, *m*-C_6H_4), 106.4 (s, $C_5(CH_3)_5$), 56.1 (s, OCH_3), 10.3 (s, $C_5(CH_3)_5$). $^{31}P\{^{1}H\}$ $\delta = 10.1$ (s). MS [31] 732 (**5e**$^+$). Anal. Calc. for $C_{32}H_{36}BF_4NO_5PRe$: C 46.95, H 4.43. Found: C 46.81, H 4.38%.

4.6. $[(\eta^5\text{-}C_5Me_5)Re(NO)(P(c\text{-}C_6H_{11})_3)(CO)]^+$ BF_4^- (**5f**$^+$ BF_4^-)

A reaction analogous to that for **5d**$^+$ BF_4^- was conducted with **4**$^+$ BF_4^- (0.101 g, 0.200 mmol), P(*c*-C_6H_{11})$_3$ (0.056 g, 0.200 mmol), and 2-butanone (15 ml). An identical workup gave **5f**$^+$ BF_4^- as a yellow powder (0.103 g, 0.138 mmol, 70%), m.p. 189–190°C [30]. ^{1}H-NMR ($CDCl_3$) [32]: $\delta = 2.18$ (s, $C_5(CH_3)_5$), 2.17–1.65, 1.45–1.15 (2m, 3C_6H_{11}). $^{13}C\{^{1}H\}$ $\delta = 204.5$ (d, $J_{CP} = 8.5$ Hz, *C*O), 105.9 (s, $C_5(CH_3)_5$), 37.6 (d, $J_{CP} = 25.5$ Hz, P*C*H), 30.7 (s, CH_2), 30.0 (d, $J_{CP} = 3.0$ Hz, CH_2), 27.3 (d, $J_{CP} = 3.0$ Hz, CH_2), 27.2 (d, $J_{CP} = 3.0$ Hz, CH_2), 26.0 (s, CH_2), 10.8 (s, $C_5(CH_3)_5$). $^{31}P\{^{1}H\}$ $\delta = 25.6$ (s). MS [31] 660 (**5f**$^+$). Anal. Calc. for $C_{29}H_{48}BF_4NO_2PRe$: C 46.65, H 6.48. Found: C 46.77, H 6.55%.

4.7. $(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(CH_3)$ (**2b**)

A Schlenk flask was charged with THF (10 ml) and **5b**$^+$ BF_4^- (0.200 g, 0.261 mmol). Then $LiEt_3BH$ (1.0 M in THF; 0.64 ml, 0.64 mmol) was added to the suspension with stirring. After 10 min, BH_3·THF (1.0 M in THF; 0.64 ml, 0.64 mmol) was added to the honey solution. After 0.5 h, solvent was removed from the red solution by oil pump vacuum. The residue was extracted with a minimum of benzene. The extract was passed through a silica gel column (2.5 × 6 cm). The solvent was removed by rotary evaporation and then oil pump vacuum to give **2b** as an orange powder (0.150 g, 0.224 mmol, 86%), m.p. 185–186°C dec. [30]. ^{1}H-NMR (C_6D_6) [32]: $\delta = 7.58$ (dd, $J_{HP} = 10.3$ Hz, $J_{HH} = 8.0$ Hz, 3*o*-C_6H_4), 6.93 (br d, $J_{HH} = 7.3$ Hz, 3*m*-C_6H_4), 2.00 (s, 3ArCH_3), 1.62 (s, $C_5(CH_3)_5$), 1.35 (d, $J_{HP} = 6.8$ Hz, ReCH_3). $^{13}C\{^{1}H\}$ $\delta = 139.5$ (s, *p*-C_6H_4), 134.4 (d, $J_{CP} = 10.8$ Hz, *o*-C_6H_4), 134.0 (d, $J_{CP} = 49.1$ Hz, *i*-C_6H_4), 129.1 (d, $J_{CP} = 10.0$ Hz, *m*-C_6H_4), 97.9 (s, $C_5(CH_3)_5$), 21.2 (s, ArCH_3), 9.9 (s, $C_5(CH_3)_5$), −22.1 (d, $J_{CP} = 6.6$ Hz, ReCH_3). $^{31}P\{^{1}H\}$ $\delta = 24.5$ (s). MS [31] 671 (**2b**$^+$). Anal. Calc. for $C_{32}H_{39}NOPRe$: C 57.29, H 5.86. Found: C 57.23, H, 5.84%.

4.8. $(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4\text{-}t\text{-}C_4H_9)_3)(CH_3)$ (**2c**)

A reaction analogous to that for **2b** was conducted with THF (10 ml), **5c**$^+$ BF_4^- (0.258 g, 0.287 mmol), $LiEt_3BH$ (1.0 M in THF; 0.70 ml, 0.70 mmol), and BH_3·THF (1.0 M in THF; 1.70 ml, 1.70 mmol). An identical workup gave **2c** as an orange powder (0.123 g, 0.154 mmol, 53%), m.p. 271–273°C dec. [30]. ^{1}H-NMR (C_6D_6) [32]: $\delta = 7.70$ (dd, $J_{HP} = 10$ Hz, $J_{HH} = 8.6$ Hz, 3*o*-C_6H_4), 7.20 (dd, $J_{HP} = 1.8$ Hz, $J_{HH} = 8.7$ Hz, 3*m*-C_6H_4), 1.62 (s, $C_5(CH_3)_5$), 1.40 (d, $J_{HP} = 6.6$ Hz, ReCH_3), 1.12 (s, 3$C(CH_3)_3$). $^{13}C\{^{1}H\}$ $\delta = 152.9$ (d, $J_{CP} = 2.0$ Hz, *p*-C_6H_4), 134.7 (d, $J_{CP} = 10.6$ Hz, *o*-C_6H_4), 134.5 (d, $J_{CP} = 50$ Hz, *i*-C_6H_4; one line at 134.1, other obscured by *o*-C_6H_4 signal), 125.7 (d, $J_{CP} = 10.0$ Hz, *m*-C_6H_4), 98.3 (s, $C_5(CH_3)_5$), 34.9 (s, $C(CH_3)_3$), 31.6 (s, $C(CH_3)_3$), 10.1 (s, $C_5(CH_3)_5$), −21.8 (d, $J_{CP} = 6.9$ Hz, ReCH_3). $^{31}P\{^{1}H\}$ $\delta = 23.2$ (s). MS [31] (**2c**$^+$). Anal. Calc. for $C_{41}H_{57}NOPRe$: C 61.78, H 7.21. Found: C 61.87, H 7.24%.

4.9. $(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4C_6H_5)_3)(CH_3)$ (**2d**)

A reaction analogous to that for **2b** was conducted with THF (10 ml), **5d**$^+$ BF_4^- (0.526 g, 0.550 mmol), $LiEt_3BH$ (1.0 M in THF; 1.40 ml, 1.40 mmol), and BH_3·THF (1.0 M in THF; 3.30 ml, 3.30 mmol). An identical workup gave **2d** as an orange powder (0.402 g, 0.470 mmol, 71%), m.p. 165–168°C dec. [30]. ^{1}H-NMR (C_6D_6) [32]: $\delta = 7.81$ (dd, $J_{HP} = 9.9$ Hz, $J_{HH} = 8.4$ Hz, 3*o*-C_6H_4), 7.50–7.39 (m, 12H of 3PAr_3), 7.23–7.08 (m, 9H of 3PAr_3), 1.66 (s, $C_5(CH_3)_5$), 1.45 (d, $J_{HP} = 6.9$ Hz, ReCH_3). $^{13}C\{^{1}H\}$ (CD_2Cl_2) $\delta = 144.8$ (d, $J_{CP} = 2.7$ Hz, *p*-C_6H_4), 142.6 (d, $J_{CP} = 2.0$ Hz, *i*-C_6H_5), 140.4 (s, *p*-C_6H_5), 134.9 (d, $J_{CP} = 10.9$ Hz, *o*-C_6H_4), 129.1 (s, *o*-C_6H_5), 128.2 (d, $J_{CP} = 46.4$ Hz, *i*-C_6H_4), 127.4 (s, *m*-C_6H_5), 127.1 (d, $J_{CP} = 10.0$ Hz, *m*-C_6H_4), 98.2 (d, $J_{CP} = 2.0$ Hz, $C_5(CH_3)_5$), 9.8 (s, $C_5(CH_3)_5$), −22.1 (d, $J_{CP} = 6.7$ Hz, ReCH_3). $^{31}P\{^{1}H\}$ (C_6D_6) $\delta = 25.6$ (s). MS [31] 857 (**2d**$^+$). Anal. Calc. for $C_{47}H_{45}NOPRe$: C 65.87, H 5.29. Found: C 65.70, H, 5.51%.

4.10. $(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4OCH_3)_3)(CH_3)$ (**2e**)

A reaction analogous to that for **2b** was conducted with THF (10 ml), **5e**$^+$ BF_4^- (0.100 g, 0.122 mmol), $LiEt_3BH$ (1.0 M in THF; 0.25 ml, 0.25 mmol), and BH_3·THF (1.0 M in THF; 0.50 ml, 0.50 mmol). An identical workup gave **2e** as an orange powder (0.044 g, 0.061 mmol, 50%), m.p. 180–181°C dec. [30]. ^{1}H-NMR (C_6D_6) [32]: $\delta = 7.60$ (dd, $J_{HP} = 10$ Hz, $J_{HH} = 8.8$ Hz, 3*o*-C_6H_4), 6.74 (dd, $J_{HP} = 1.2$ Hz, $J_{HH} = 8.8$ Hz, 3*m*-C_6H_4), 3.22 (s, 3OCH_3), 1.64 (s, $C_5(CH_3)_5$), 1.41 (d, $J_{HP} = 6.7$ Hz, ReCH_3). $^{13}C\{^{1}H\}$ $\delta = 161.4$ (s, *p*-C_6H_4), 136.2 (br s, *o*-C_6H_4), 129.1 (d, $J_{CP} = 52$ Hz, *i*-C_6H_4), 114.3 (d, $J_{CP} = 9.6$ Hz, *m*-C_6H_4), 98.3 (s, $C_5(CH_3)_5$), 55.1 (s, $\mathrm{OCH_3}$), 10.4 (s, $\mathrm{C_5(\mathit{C}H_3)_5}$), -21.6 (d, $J_{\mathrm{CP}} = 7.0$ Hz, $\mathrm{Re\mathit{C}H_3}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ $\delta = 21.9$ (s). MS [31] 719 (**2e**$^+$). Anal. Calc. for $\mathrm{C_{32}H_{39}NO_4PRe}$: C 53.47, H 5.47. Found: C 53.33, H 5.44%.

4.11. *(η^5-C_5Me_5)Re(NO)(P(c-C_6H_{11})$_3$)(CH_3)* (**2f**)

A reaction analogous to that for **2b** was conducted with THF (10 ml), **5f**$^+$ $\mathrm{BF_4^-}$ (0.374 g, 0.500 mmol), $\mathrm{LiEt_3BH}$ (1.0 M in THF; 0.50 ml, 0.50 mmol), and $\mathrm{BH_3{\cdot}THF}$ (1.0 M in THF; 1.00 ml, 1.00 mmol). An identical workup gave **2f** as an orange powder (0.210 g, 0.325 mmol, 65%), m.p. 169–171°C [30]. ^{1}H-NMR ($\mathrm{CDCl_3}$) [32]: $\delta = 1.85$ (s, $\mathrm{C_5(C\mathit{H}_3)_5}$), 2.15–1.60, 1.55–1.30 (2m, $\mathrm{3C_6\mathit{H}_{11}}$), 0.73 (br s, $\mathrm{ReC\mathit{H}_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ $\delta = 97.4$ (s, $\mathrm{\mathit{C}_5\ (CH_3)_5}$), 36.9 (d, $J_{\mathrm{CP}} = 23.2$ Hz, $\mathrm{P\mathit{C}H}$), 30.1 (s, $\mathrm{\mathit{C}H_2}$), 29.5 (s, $\mathrm{\mathit{C}H_2}$), 28.0, 27.8, 27.7 (overlapping d, $\mathrm{2\mathit{C}H_2}$), 26.8 (s, $\mathrm{\mathit{C}H_2}$), 10.6 (s, $\mathrm{C_5(\mathit{C}H_3)_5}$), -27.3 (d, $J_{\mathrm{CP}} = 8.7$ Hz; $\mathrm{Re\mathit{C}H_3}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ $\delta = 18.5$ (s). MS [31] 647 (**2f**$^+$). Anal. Calc. for $\mathrm{C_{29}H_{51}NOPRe}$: C 53.84, H 7.95. Found: C 53.48, H 7.79%.

4.12. *(η^5-C_5Me_5)Re(NO)(η^2-TCNE)(CH_3)* (**6**)

A Schlenk flask was charged with **2a** (0.063 g, 0.10 mmol) [7] and benzene (10 ml). A solution of TCNE (0.013 g, 0.010 mmol) in benzene (10 ml) was slowly added with stirring [28]. After 1 h, the solvent was removed by oil pump vacuum. The residue was washed with hexane (2 × 5 ml) and $\mathrm{Et_2O}$ (5 ml), and dissolved in a minimum of $\mathrm{CH_2Cl_2}$. The solution was layered with hexane. After 24 h, the dark yellow blocks were collected by filtration and dried by oil pump vacuum to give **6** (0.040 g, 0.081 mmol, 81%), m.p. 232–235°C dec. IR ($\mathrm{CH_2Cl_2}$): $\nu_{\mathrm{C\equiv N}} = 2234\ \mathrm{cm^{-1}}$ w $\nu_{\mathrm{NO}} = 1753$ s. ^{1}H-NMR [32] ($\mathrm{CD_3CN}$): $\delta = 2.01$ (s, $\mathrm{C_5(C\mathit{H}_3)_5}$), 1.49 (s, $\mathrm{ReC\mathit{H}_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ ($\mathrm{CD_2Cl_2}$): $\delta = 115.2$, 115.1, 113.4, 113.2 (4s, $\mathrm{4\mathit{C}N}$), 110.0 (s, $\mathrm{\mathit{C}_5(CH_3)_5}$), 22.0, 11.0 (2s, $\mathrm{2\mathit{C}CN}$), 9.1 (s, $\mathrm{C_5(\mathit{C}H_3)_5}$), 0.88 (s, $\mathrm{Re\mathit{C}H_3}$). MS [31] 496 (**6**$^+$). Anal. Calc. for $\mathrm{C_{17}H_{18}N_5ORe}$: C 41.29, H 3.67. Found: C 41.48, H 3.61%.

4.13. *Crystallography*

Data were collected on **6** as outlined in Table 2. The space group was determined from a Laue symmetry check and systematic absences, and confirmed by subsequent refinement. Lorentz and polarization (but no absorption) corrections were applied. The structure was solved by Patterson methods and expanded by Fourier difference techniques. This model was refined by full-matrix least-squares analysis on F, with all atoms anisotropic. Hydrogen atom positions were calculated. Scattering factors were taken from the literature. Anomalous dispersion effects were included in F_{c}. Calculations were performed on a Silicon-Graphics computer, using the TEXSAN software package.

5. Supplementary material

Atomic coordinates and other data for **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC no. 140673. Copies of this information can be obtained free on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[32] NMR data were recorded on Varian 300 MHz spectrometers ($^1H/^{13}C/^{31}P$ 300/75.5/121 MHz). Chemical shifts are given versus internal or external standards. The 4-PC_6H_4X ^{13}C and ^1H-NMR signals are given relative to the phosphorus substituent ($i/o/m/p$).