



Reactions of rhenium and manganese carbonyl complexes with 1,8-bis(diphenylphosphino)naphthalene: Ligand chelation, C–H and C–P bond-cleavage reactions

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ABSTRACT

Reaction of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with 1,8-bis(diphenylphosphino)naphthalene (dppn) afforded three mono-rhenium complexes *fac*- $[\text{Re}(\text{CO})_3(\kappa^1:\eta^1\text{-PPh}_2\text{C}_{10}\text{H}_6)(\text{PPh}_2\text{H})]$ (**1**), *fac*- $[\text{Re}(\text{CO})_3(\kappa^1:\kappa^1:\eta^1\text{-}(\text{O})\text{PPh}_2\text{C}_{10}\text{H}_6(\text{O})\text{PPh}(\text{C}_6\text{H}_4))]$ (**2**) and *fac*- $[\text{ReCl}(\text{CO})_3(\kappa^2\text{-PPh}_2\text{C}_{10}\text{H}_6\text{PPh}_2)]$ (**3**). Compounds **1–3** are formed by Re–Re bond cleavage and P–C and C–H bond activation of the dppn ligand. Each of these three complexes have three CO groups arranged in *facial* fashion. Compound **1** contains a chelating cyclometalated diphenylphosphino ligand and a terminally coordinated PPh₂H ligand. Compound **2** consists of an orthometalated dppn-dioxide ligand coordinated in a $\kappa^1:\kappa^1:\eta^1$ -fashion via both the oxygen atoms and *ortho*-carbon atom of one of the phenyl rings. Compound **3** consists of an unchanged chelating dppn ligand and a terminal Cl ligand. Treatment of $[\text{Mn}_2(\text{CO})_8(\text{MeCN})_2]$ with a slight excess of dppn in refluxing toluene at 72 °C, gave the previously reported $[\text{Mn}_2(\text{CO})_8(\mu\text{-PPh}_2)_2]$ (**4**), formed by cleavage of C–P bonds, and the new compound *fac*- $[\text{MnCl}(\text{CO})_3(\kappa^2\text{-PPh}_2\text{C}_{10}\text{H}_6\text{PPh}_2)]$ (**5**), which has an unaltered chelating dppn and a terminal Cl ligand. In sharp contrast, reaction of $[\text{Mn}_2(\text{CO})_8(\text{MeCN})_2]$ with slight excess of dppn at room temperature yielded the dimanganese $[\text{Mn}_2(\text{CO})_9(\kappa^1\text{-PPh}_2(\text{C}_{10}\text{H}_7))]$ (**6**) in which the diphenylphosphino ligand, formed by facile cleavage of one of the P–C bonds, is axially coordinated to one Mn atom. Compound **6** was also obtained from the reaction of $[\text{Mn}_2(\text{CO})_9(\text{MeCN})]$ with dppn at room temperature. The XRD structures of complexes **1–3**, **5**, **6** are reported.

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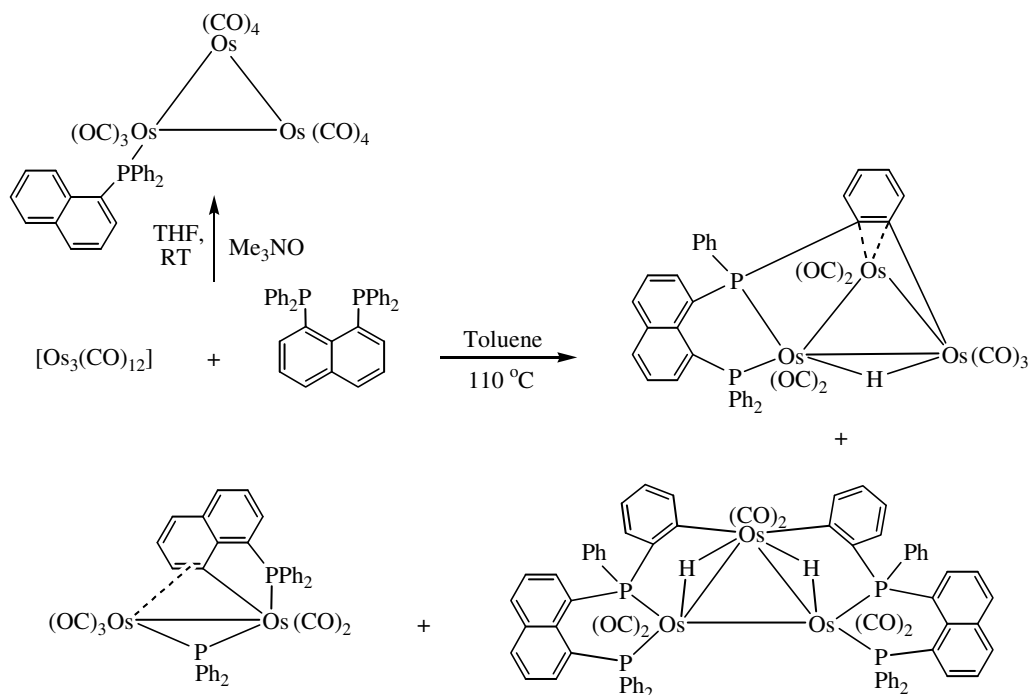
1. Introduction

The synthesis and reactivity of transition metal carbonyl complexes bearing diphosphine ligands continue to excite interest, both from a synthetic point of view due to their potential applicability to effect organic transformations [1–4], and their possible involvement in homogeneous catalytic processes [5,6]. Late transition metal systems with chelating diphosphine ligands such as 1,8-bis(diphenylphosphino)naphthalene with a rigid C₃-backbone [7,8] have been reported to be active catalysts in CO/ethylene co-polymerization [9]. The reactivity of this ligand with polynuclear transition metal carbonyl compounds have been recently investigated by the Bruce [10–12] and Richmond [13,14] research groups. For

example, Bruce and coworkers reported three tetraruthenium compounds, $[\text{Ru}_4(\mu\text{-H})(\mu\text{-CO})_3(\text{CO})_7\{\mu_3\text{-PPh}_2(\text{nap})\text{PPh}(\text{C}_6\text{H}_4)\}]$, $[\text{Ru}_4(\mu\text{-H})(\text{CO})_{11}(\mu_3\text{-C}_6\text{H}_4)\{\mu\text{-PPh}(\text{nap})\text{PPh}_2\}]$, and $[\text{Ru}_4(\mu\text{-CO})(\text{CO})_9(\mu_4\text{-C}_6\text{H}_4)\{\mu_4\text{-P}(\text{nap})\text{PPh}_2\}]$ and one triruthenium compound $[\text{Ru}_3(\mu\text{-H})(\text{CO})_8\{\mu_3\text{-PPh}_2(\text{nap})\text{PPh}(\text{C}_6\text{H}_4)\}]$ (nap = 1,8-C₁₀H₆) from reactions of $[\text{Ru}_3(\text{CO})_{12}]$ and 1,8-bis(diphenylphosphino)naphthalene at elevated temperatures [10]. These compounds were formed by the aryl C–H and C–P bond-cleavage reactions of the ligand. They also reported that $[\text{Os}_3(\text{CO})_{12}]$ reacts with 1,8-bis(diphenylphosphino)naphthalene at 110 °C to give the triosmium compounds $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_6\{\mu_3\text{-PPh}_2(\text{nap})\text{PPh}(\text{C}_6\text{H}_4)\}_2]$ and $[\text{Os}_3(\mu\text{-H})(\text{CO})_8\{\mu_3\text{-PPh}_2(\text{nap})\text{PPh}(\text{C}_6\text{H}_4)\}]$, and the dinuclear $[\text{Os}_2(\text{CO})_5(\mu\text{-PPh}_2)(\mu\text{-PPh}_2(\text{nap}))]$ (Scheme 1) [11]. The triosmium compounds are formed by metallation of a Ph group of dppn, while the dinuclear compound is formed by cleavage of a C–P bond of the ligand. With a view to restrict the subsequent reactions to the C₁₀ ring,

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Scheme 1.

they investigated the reactions of 1,8-bis(dimethylphosphino)naphthalene with $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$ and obtained $[\text{Ru}_3(\text{CO})_{12-n}\{\text{PMe}_2(\text{nap})\}_n]$ ($n = 1-3$) and $[\text{Ru}_3(\text{CO})_9(\mu\text{-dppm})\{\text{PMe}_2(\text{nap})\}]$, respectively [12]. However, it is interesting to note that a cluster containing an unaltered dppn ligand was not detected in any of the above reactions. Very recently, Richmond et al. have investigated the reactions of 1,8-bis(diphenylphosphino)naphthalene with the hydride-bridged ruthenium cluster $[\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}]$ and the cobalt cluster $[\text{PhCCo}_3(\text{CO})_9]$ and obtained products containing both unaltered and activated dppn ligands [13,14]. For instance, the ruthenium cluster afforded $[\text{Ru}_3(\mu\text{-H})_4(\text{CO})_{10}(\kappa^2\text{-dppn})]$ as the sole isolable product [13]; whereas the cobalt cluster yielded $[\text{PhCCo}_3(\text{CO})_8(\mu\text{-C}_{10}\text{H}_7)]$ and $[\text{PhCCo}_3(\text{CO})_4(\mu\text{-CO})_3(\kappa^2\text{-dppn})]$ [14] under the same experimental conditions. To our knowledge, however, no examples have been reported in the literature concerning the reactivity between 1,8-bis(diphenylphosphino)naphthalene and group 7 transition metal carbonyl complexes. We thus decided to investigate the reactivity of 1,8-bis(diphenylphosphino)naphthalene with the labile complexes $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$, $[\text{Mn}_2(\text{CO})_9(\text{MeCN})]$ and $[\text{Mn}_2(\text{CO})_8(\text{MeCN})_2]$ and the results are described in the present paper.

2. Experimental

All the reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use by standard methods. Bis(diphenylphosphino)naphthalene (dppn), a gift from Prof. Michael G. Richmond, was prepared according to the known method [15] and used as received. $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ was purchased from Lancaster and water was removed using a Dean-Stark apparatus by azeotropic distillation from benzene and the anhydrous Me_3NO was stored under nitrogen. The starting complexes $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ [16], $[\text{Mn}_2(\text{CO})_9(\text{MeCN})]$ [17] and $[\text{Mn}_2(\text{CO})_8(\text{MeCN})_2]$ [17] were prepared according to published procedures. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. ^1H NMR spectra were

recorded on a Bruker DPX 400 spectrometer. Elemental analyses were performed by BCSIR Laboratories, Dhaka. Fast atom bombardment mass spectra were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant.

2.1. Reaction of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with dppn

A toluene solution (35 mL) of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ (150 mg, 0.15 mmol) and dppn (150 mg, 0.30 mmol) was heated to reflux for 1 h and 15 min. The solvent was removed by rotary evaporation and the residue chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (4:1, v/v) developed three bands. The first band gave *fac*- $[\text{Re}(\text{CO})_3(\kappa^1:\eta^1\text{-PPh}_2\text{C}_{10}\text{H}_6)(\text{PPh}_2\text{H})]$ (**1**) (23 mg, 14%) as colorless crystals after recrystallization from hexane/ CH_2Cl_2 at 4 °C. Anal. Calc. for $\text{C}_{37}\text{H}_{27}\text{O}_3\text{P}_2\text{Re}$: C, 57.88; H, 3.54. Found: C, 58.22; H, 3.71%. IR (ν_{CO} , CH_2Cl_2): 2011 vs, 1942 vs, 1900 vs cm^{-1} . ^1H NMR (CDCl_3): δ 7.92 (d, $J = 7.8$ Hz, 1H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.52 (d, $J = 7.8$ Hz, 1H), 7.45 (m, 7H), 7.32 (m, 4H), 7.21 (m, 3H), 6.97 (m, 7H), 6.52 (d, $J = 7.4$ Hz, 1H), 6.49 (d, $J = 7.4$ Hz, 1H), 4.92 (dd, $J_{\text{P-H}} = 357.1$, 9.3 Hz, 1H). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ 31.5 (s), 1.7 (s). MS (FAB): m/z 768 (M^+). The second band afforded *fac*- $[\text{Re}(\text{CO})_3(\kappa^1:\kappa^1:\eta^1\text{-OPPh}_2\text{C}_{10}\text{H}_6\text{OPPh}(\text{C}_6\text{H}_4))]$ (**2**) (19 mg, 11%) as colorless crystals after recrystallization from hexane/ CH_2Cl_2 at 4 °C. Anal. Calc. for $\text{C}_{37}\text{H}_{25}\text{O}_5\text{P}_2\text{Re}$: C, 55.71; H, 3.16. Found: C, 55.92; H, 3.34%. IR (ν_{CO} , CH_2Cl_2): 1998 vs, 1881 vs, 1860 vs cm^{-1} . ^1H NMR (CDCl_3): δ 8.07 (m, 2H), 7.89 (m, 2H), 7.65 (d, $J = 7.2$ Hz, 1H), 7.60 (d, $J = 7.2$ Hz, 1H), 7.35 (t, $J = 7.2$ Hz, 1H), 7.37 (m, 4H), 7.21 (m, 9H), 7.17 (t, $J = 7.2$ Hz, 1H), 6.84 (d, $J = 6.4$ Hz, 1H), 6.81 (d, $J = 7.4$ Hz, 1H), 6.74 (m, 1H), 6.65 (t, $J = 7.2$ Hz, 1H). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ 69.0 (s), 38.7 (s). MS (FAB): m/z 798 (M^+). The third band yielded *fac*- $[\text{Re}(\text{Cl})(\text{CO})_3(\text{PPh}_2\text{C}_{10}\text{H}_6\text{PPh}_2)]$ (**3**) (71 mg, 40%) as colorless crystals after recrystallization from hexane/ CH_2Cl_2 at 4 °C. Anal. Calc. for $\text{C}_{37}\text{H}_{26}\text{O}_3\text{Cl}_1\text{P}_2\text{Re}_2$: C, 55.40; H, 3.27. Found: C, 55.67; H, 3.38%. IR (ν_{CO} , CH_2Cl_2): 2070 s, 2012 vs, 1966 s cm^{-1} . ^1H NMR (CDCl_3): δ 8.05 (m, 2H), 7.63 (m, 4H), 7.37 (m, 10H), 7.11 (t, $J = 7.2$ Hz, 2H),

6.96 (t, $J = 7.2$ Hz, 4H), 6.83 (m, 4H). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ 8.9(s). MS (FAB): m/z 802 (M^+).

2.2. Reaction of $[\text{Mn}_2(\text{CO})_8(\text{MeCN})_2]$ with *dppn*

2.2.1. At 72 °C

A toluene solution (35 mL) of $[\text{Mn}_2(\text{CO})_8(\text{MeCN})_2]$ (180 mg, 0.43 mmol) and *dppn* (215 mg, 0.43 mmol) was heated at 72 °C for 5 h. After removal of the solvent under reduced pressure, the residue was chromatographed as above to develop two bands. The first band gave the known compound $[\text{Mn}_2(\text{CO})_8(\mu\text{-PPh}_2)_2]$ (**4**) (29 mg, 10%) as pale yellow crystals after recrystallization from hexane/ CH_2Cl_2 at 4 °C. The second band afforded *fac*- $[\text{Mn}(\text{Cl})(\text{CO})_3(\kappa^1\text{-PPh}_2\text{C}_{10}\text{H}_6\text{PPh}_2)]$ (**5**) (66 mg, 23%) as colorless crystals after recrystallization from hexane/ CH_2Cl_2 at 4 °C. Anal. Calc. for $\text{C}_{37}\text{H}_{26}\text{ClO}_3\text{Mn}_2\text{P}_2$: C, 66.23; H, 3.91. Found: C, 66.39; H, 4.24%. IR (ν_{CO} , CH_2Cl_2): 2067 s, 2013 vs, 1968 s cm^{-1} . ^1H NMR (CDCl_3): δ 8.04 (m, 2H), 7.79 (m, 4H), 7.39 (m, 10H), 7.11 (m, 2H), 6.95 (m, 4H), 6.86 (m, 4H). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ 49.3 (s). MS (FAB): m/z 670 (M^+).

2.2.2. At room temperature

A CH_2Cl_2 solution (50 mL) of $[\text{Mn}_2(\text{CO})_8(\text{MeCN})_2]$ (160 mg, 0.38 mmol) and *dppn* (191 mg, 0.38 mmol) was stirred at room temperature for 45 h. The solvent was removed under reduced pressure and the residue chromatographed as above to give one major and several minor bands. The major band gave $[\text{Mn}_2(\text{CO})_9\{\kappa^1\text{-PPh}_2(\text{C}_{10}\text{H}_7)\}]$ (**6**) (30 mg, 12%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at 4 °C. Anal. Calc. for $\text{C}_{31}\text{H}_{17}\text{O}_9\text{Mn}_2\text{P}$: C, 55.22; H, 2.54. Found: C, 55.40; H, 2.76%. IR (ν_{CO} , CH_2Cl_2): 2090 s, 2009 s, 1992 vs, 1967 m, 1933 m cm^{-1} . ^1H NMR (CDCl_3): δ 7.94–7.83 (m, 5H), 7.62–7.43 (m, 12H). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ 74.3 (s). MS (FAB): m/z 674 (M^+). The contents of the minor bands were too small for complete characterization.

2.3. Reaction of $[\text{Mn}_2(\text{CO})_9(\text{MeCN})]$ with *dppn*

A CH_2Cl_2 solution (30 mL) of $[\text{Mn}_2(\text{CO})_9(\text{MeCN})]$ (160 mg, 0.40 mmol) and *dppn* (198 mg, 0.40 mmol) was stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (7:3, v/v) developed four bands. The last band was unreacted starting material while the second band gave $[\text{Mn}_2(\text{CO})_9\{\kappa^1\text{-PPh}_2(\text{C}_{10}\text{H}_7)\}]$ (**6**) (35 mg, 27%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at 4 °C. The other two bands gave too little product for complete characterization.

2.4. X-ray structure determinations

Single crystals were mounted on fibres and diffraction data collected at low temperature (see Table 1) on Bruker AXS SMART APEX CCD diffractometers using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Data collection, indexing and initial cell refinements were all done using SMART [18] software. Data reduction were done with SAINT [19] software and the SADABS programme [20] was used to apply empirical absorption corrections. The structures were solved by direct methods [21] and refined by full-matrix least-squares [22]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included using a riding model. Scattering factors were taken from International Tables for X-ray Crystallography [23]. Additional details of data collection and structure refinement are given in Table 1.

3. Results and discussion

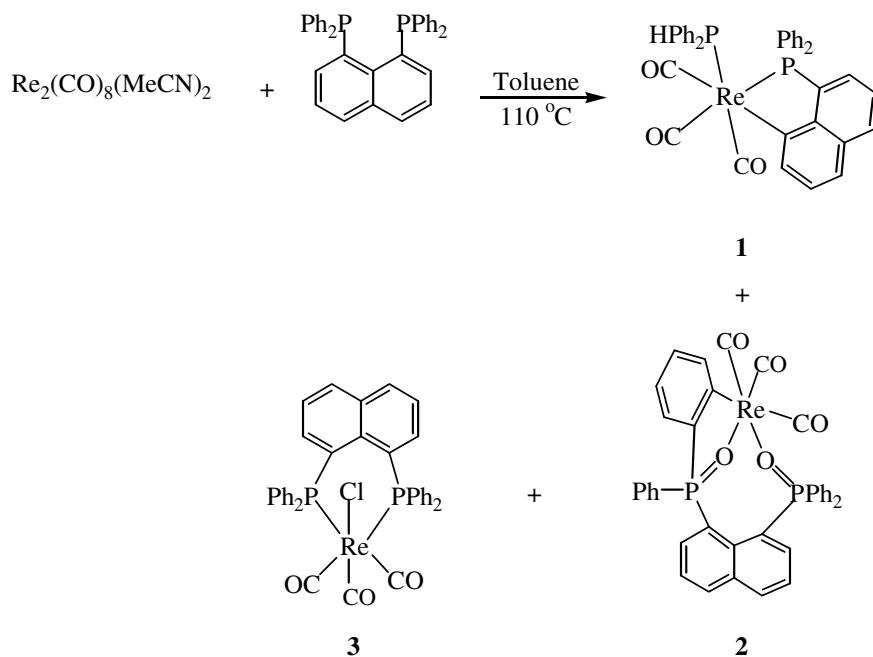
3.1. Formation of mononuclear rhenium complexes by C–P and C–H bond activation in *dppn*

Treatment of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with two equivalents of *dppn* in refluxing toluene, followed by chromatographic separation, lead

Table 1
Crystallographic data and structure refinement^a for **1**, **2**, **3**, **5** and **6**

	1	2	3	5	6
Empirical formula	$\text{C}_{37}\text{H}_{27}\text{O}_3\text{P}_2\text{Re}$	$\text{C}_{38}\text{H}_{27}\text{Cl}_2\text{O}_3\text{P}_2\text{Re}$	$\text{C}_{37}\text{H}_{26}\text{ClO}_3\text{P}_2\text{Re}$	$\text{C}_{37}\text{H}_{26}\text{ClMnO}_3\text{P}_2$	$\text{C}_{31}\text{H}_{17}\text{Mn}_2\text{O}_9\text{P}$
Formula weight	767.73	882.64	802.17	670.91	674.30
<i>T</i> (K)	100(2)	150(2)	173(2)	293(2)	150(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> (Å)	19.1751(3)	10.8628(8)	10.4072(4)	10.2672(6)	15.9421(12)
<i>b</i> (Å)	18.7407(3)	11.8435(9)	14.9325(5)	14.7815(9)	18.0361(14)
<i>c</i> (Å)	18.4101(3)	14.0293(11)	20.3603(7)	20.0466(12)	19.8983(15)
α (°)	90	94.7370(10)	83.187(2)	83.1140(10)	90
β (°)	113.0020(10)	109.1060(10)	88.310(2)	88.3270(10)	90
γ (°)	90	90.7270(10)	86.761(2)	86.7250(10)	90
Volume (Å ³)	6089.74(17)	1698.2(2)	3135.91(19)	3014.7(3)	5721.4(8)
<i>Z</i>	8	2	4	4	8
<i>D</i> _{calc} (Mg/m ³)	1.675	1.726	1.699	1.478	1.566
μ (Mo $K\alpha$) (mm ⁻¹)	9.093	3.874	9.625	0.671	0.994
<i>F</i> (000)	3024	868	1576	1376	2720
Crystal size (mm ³)	0.20 × 0.14 × 0.12	0.44 × 0.40 × 0.34	0.28 × 0.16 × 0.13	0.46 × 0.24 × 0.08	0.44 × 0.42 × 0.12
θ Range (°)	3.44–61.41	1.73–28.26	2.19–65.75	1.39–28.26	1.99–28.29
Index ranges	–21 ≤ <i>h</i> ≤ 19 0 ≤ <i>k</i> ≤ 20 0 ≤ <i>l</i> ≤ 20	–14 ≤ <i>h</i> ≤ 14 –15 ≤ <i>k</i> ≤ 15 –18 ≤ <i>l</i> ≤ 18	–11 ≤ <i>h</i> ≤ 10 –17 ≤ <i>k</i> ≤ 17 –23 ≤ <i>l</i> ≤ 23	–13 ≤ <i>h</i> ≤ 13 –19 ≤ <i>k</i> ≤ 19 –26 ≤ <i>l</i> ≤ 26	–20 ≤ <i>h</i> ≤ 21 –23 ≤ <i>k</i> ≤ 23 –26 ≤ <i>l</i> ≤ 26
Reflections collected	25 134	15 004	14 154	26 782	48 038
Independent reflections [<i>R</i> (int)]	4565 [0.0253]	7794 [0.0210]	6165 [0.0166]	13 880 [0.0245]	6974 [0.0299]
Maximum and minimum transformation	0.4083 and 0.2635	0.3526 and 0.2805	0.3676 and 0.1736	0.9483 and 0.7477	0.6688 and 0.8900
Data/restraints/parameters	4565/36/471	7794/0/434	6165/0/788	13 880/0/793	6974/0/388
Goodness-of-fit on <i>F</i> ²	1.166	1.030	1.122	1.036	1.037
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0196 <i>wR</i> ₂ = 0.0484	<i>R</i> ₁ = 0.0250 <i>wR</i> ₂ = 0.0621	<i>R</i> ₁ = 0.0589 <i>wR</i> ₂ = 0.1635	<i>R</i> ₁ = 0.0429 <i>wR</i> ₂ = 0.1001	<i>R</i> ₁ = 0.0302 <i>wR</i> ₂ = 0.0741
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0198 <i>wR</i> ₂ = 0.0485	<i>R</i> ₁ = 0.0258 <i>wR</i> ₂ = 0.0625	<i>R</i> ₁ = 0.0735 <i>wR</i> ₂ = 0.2149	<i>R</i> ₁ = 0.0556 <i>wR</i> ₂ = 0.1064	<i>R</i> ₁ = 0.0355 <i>wR</i> ₂ = 0.0768
Largest difference peak and hole (e Å ⁻³)	0.666 and –0.378	1.492 and –1.736	1.346 and –3.245	0.592 and –0.454	0.439 and –0.214

^a Details in common: X-radiation, Mo $K\alpha$ ($\lambda = 0.71073$ Å), refinement method: full-matrix least-squares on *F*².



Scheme 2.

to the formation of three new compounds $\text{fac}[\text{Re}(\text{CO})_3(\kappa^1:\eta^1\text{-PPh}_2\text{C}_{10}\text{H}_6)(\text{PPh}_2\text{H})]$ (**1**), $\text{fac}[\text{Re}(\text{CO})_3\{\kappa^1:\kappa^1:\eta^1\text{-OPPh}_2\text{C}_{10}\text{H}_6\text{OPPh}(\text{C}_6\text{H}_4)\}]$ (**2**) and $\text{fac}[\text{Re}(\text{Cl})(\text{CO})_3(\text{PPh}_2\text{C}_{10}\text{H}_6\text{PPh}_2)]$ (**3**) in 14%, 11% and 40% yields, respectively (Scheme 2). All compounds have been characterized by a combination of IR, NMR, mass spectral data, elemental analysis and single crystal X-ray diffraction studies. Formation of these mononuclear compounds (**1–3**) may proceed from $[\text{Re}_2(\text{CO})_8(\text{MeCN})(\text{dppn})]$ which can undergo bond cleavage forming $[\text{Re}(\text{CO})_4(\text{dppn})]$ and $[\text{Re}(\text{CO})_4(\text{MeCN})]$. The later compound can reform the dimer and the former compound can give compound **1** by C–P bond cleavage of the chelating dppn with cyclometalation of the naphthyl group at C(1) (Fig. 1) and loss of one CO ligand. The hydride of PPh_2H comes from the formation of compound **2** with orthometallation to Re of a phenyl group of PPh_2 . Also O_2 insertion (oxidative addition) between the Re–P bonds followed by Re–C(1) bond cleavage and P–C(1) (Fig. 1) bond formation yields compound **2**.

The molecular structure of **1** is shown in Fig. 1 and selected bond distances and angles are listed in the caption. The compound contains a single rhenium atom with three carbonyl groups, a diphenylphosphine and a cyclometalated naphthyl-diphenylphosphine ligand. The coordination geometry at the Re atom is a distorted octahedron with three carbonyl ligands arranged in a *facial* fashion. The distortion from octahedral coordination geometry is evident from reduction of the C–Re–P angle from 90° in the idealized polyhedron to $79.04(8)^\circ$ in **1**. The *trans* angles about rhenium range from $168.62(9)^\circ$ to $172.48(9)^\circ$ which are comparable to the corresponding angles in $\text{fac}[\text{ReCl}(\text{CO})_3\{\kappa^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)\}_2]$ {range from $175.44(14)^\circ$ to $178.99(13)^\circ$ } [24] and $\text{fac}[\text{ReCl}(\text{CO})_3\{\kappa^1\text{-NC}_3\text{H}_3\text{S}\}]$ {range from $174.44(18)^\circ$ to $179.27(19)^\circ$ } [25].

The Re(1)–C(1) bond distance {2.225(3) Å} is shorter than those observed in Re–cyclopentadienyl complexes {2.245–2.405 Å} [26]. The Re–P bond distances {Re(1)–P(1) = 2.4204(7) and Re(1)–P(2) = 2.4456(7) Å} are comparable to the Re–P bond distances in $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})]$ {2.457(4) $^\circ$, 2.449(4) $^\circ$ } [27]. The five-membered chelate metallacycle ring is nearly coplanar and the orientation of the phenyl rings is unusual and presumably would not persist in solution. The carbonyl groups assume a *fac* geometry with a longer average Re–CO bond distance of 1.950(9) Å than

the average Re–CO bond distances in $\text{fac}[\text{ReCl}(\text{CO})_3\{\kappa^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)\}_2]$ {1.917(3) Å} and $\text{fac}[\text{ReCl}(\text{CO})_3\{\kappa^1\text{-NC}_3\text{H}_3\text{S}\}_2]$ {1.914(7) Å} [24,25].

The spectroscopic data of **1** are consistent with the solid-state structure. The infrared spectrum display three bands in the carbonyl stretching region indicating the *fac* arrangement of the carbonyls, similar to those observed for $\text{fac}[\text{Re}(\text{CO})_3\text{L}_2\text{X}]$ type compounds [24–28]. In addition to the usual phenyl and naphthyl

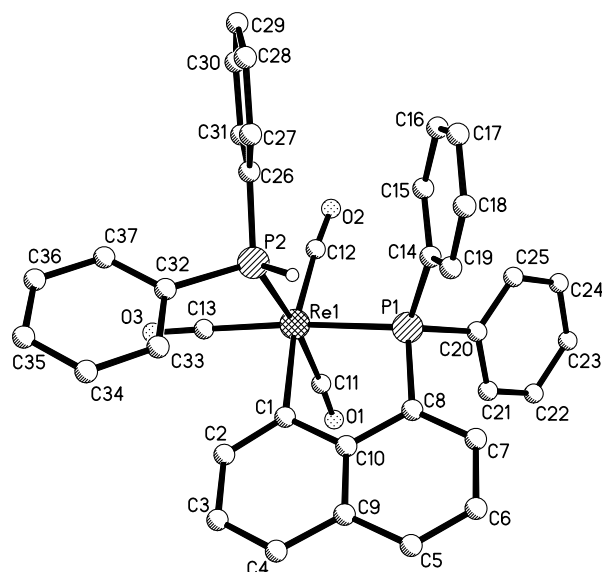


Fig. 1. Molecular structure of $\text{fac}[\text{Re}(\text{CO})_3(\kappa^1:\eta^1\text{-PPh}_2\text{C}_{10}\text{H}_6)(\text{PPh}_2\text{H})]$ **1** showing 50% probability thermal ellipsoids. Hydrogen atoms except the one attached to the phosphorus atom are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Re(1)–P(1) = 2.4204(7), Re(1)–P(2) = 2.4456(7), Re(1)–C(1) = 2.225(3), Re(1)–C(11) = 1.941(3), Re(1)–C(12) = 1.951(3), Re(1)–C(13) = 1.960(3), C(1)–Re(1)–P(1) = 79.04(8), C(1)–Re(1)–P(2) = 82.67(7), P(1)–Re(1)–P(2) = 87.95(2), C(11)–Re(1)–C(1) = 86.02(11), C(12)–Re(1)–C(1) = 171.91(11), C(13)–Re(1)–C(1) = 93.81(12), C(11)–Re(1)–P(1) = 91.19(9), C(12)–Re(1)–P(1) = 92.98(9), C(13)–Re(1)–P(1) = 172.48(9).

proton resonances in the aromatic region δ 7.92–6.50, the ^1H NMR spectrum shows a doublet of doublets at δ 4.93 (integrating to 1H) assigned to the PH proton of the diphenylphosphine ligand. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays two equal intensity singlets at δ 31.5 and 1.7, assigned to the cyclometalated naphthylidiphenylphosphine and diphenylphosphine ligands, respectively. The mass spectrum of **1** shows a molecular ion at m/z 768 together with fragmentation peaks due to the successive loss of three carbonyl groups.

The molecular structure of **2** is shown in Fig. 2 and selected bond distances and angles are listed in caption. The compound contains a single rhenium atom with three carbonyl groups and an orthometalated bis(diphenylphosphino)naphthalenedioxide ligand. The coordination geometry at the Re atom is also a distorted octahedron with three carbonyl ligands arranged in a *facial* fashion. The distortion from octahedral coordination geometry is evident from reduction of the O–Re–O angle from 90° in the idealized polyhedron to $74.12(8)^\circ$ in **2**. An interesting feature of the structure is the coordination of the dppn-dioxide through both the oxygen atoms as well as the orthometalated ligand. To the best of our knowledge, such a transformation of dppn on a metal center is unprecedented. In order to allow the oxygen atoms to be coordinated to the Re center the naphthalene unit is considerably distorted (deviations from planarity in the range ± 0.3 Å) in comparison to the free ligand. The phosphorus atoms lie -0.97 Å, P(1) and 1.11 Å, P(2) outside the least-squares plane of the naphthalene ring system, the torsion angle P(1)–C(16)–C(22)–P(2) is 54.5° . The Re–C bond distance, $2.169(3)$ Å, is significantly shorter than those observed in **1**. The Re–O bond distances, Re(1)–O(5) $2.175(2)$, Re(1)–O(4) $2.197(2)$ Å, are comparable to the Re–O bond distance, $2.203(6)$ Å, in $\text{Re}(\text{CO})_4[\mu\text{-}(E)\text{-RC}=\text{C}(\text{CO}_2\text{Et})]\text{Re}(\text{CO})_4$ [29].

The spectroscopic data of **2** are fully consistent with the solid-state structure. The pattern of the infrared spectrum of **2** in the carbonyl region is very similar to those of the *fac*- $[\text{Re}(\text{CO})_3\text{L}_2\text{X}]$ type compounds which have been characterized by X-ray diffraction studies [29–33]. The aromatic region of the ^1H NMR spectrum contains five multiplets at δ 8.07, 7.89, 7.57–7.38, 7.21 and 6.85–6.69 are due to the phenyl and naphthyl ring protons of the oxygenated dppn ligand besides this two doublets at δ 7.65 and 7.60 and two

apparent triplets at δ 7.17 and 6.65 (each integrating to 1H), assignable to the orthometalated phenyl ring. As expected the $^{31}\text{P}\{^1\text{H}\}$ NMR exhibits two equal intensity singlets at δ 69.0 and 38.6 indicating that the ^{31}P nuclei are non-equivalent. The mass spectrum contains the appropriate molecular ion peak (M^+) for the molecular mass of 798 Da.

Complex **3** crystallized with two molecules per asymmetric unit. All molecules in the structure are separated by normal van der Waals distances and there are no anomalously close intermolecular contacts. The respective bond lengths and angles in the two molecules show only minor variations. The structure of one of these molecules is shown in Fig. 3 and selected bond distances are listed in the caption. The molecule consists of a single rhenium atom with three carbonyl groups, a chelating dppn ligand and a terminally coordinated Cl ligand, which was contributed by the solvent (CH_2Cl_2). The coordination geometry of the Re atom can be described as a distorted octahedron with three carbonyl ligands arranged in a *facial* fashion. The distortion from octahedral coordination geometry is evident from reduction of the P–Re–P angle from 90° in the idealized polyhedron to $82.50(11)^\circ$ in **3** which is comparable with the P–Mo–P angle $\{81.267(13)^\circ\}$ in $[\text{Mo}_2(\text{CO})_4(\text{dppn})]$ [30]. The basic structure of **3** is very similar to that of the recently reported single rhenium compounds *fac*- $[\text{ReCl}(\text{CO})_3\{\kappa^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)_2\}]$ [24] and *fac*- $[\text{ReCl}(\text{CO})_3\{\kappa^1\text{-C}_3\text{H}_3\text{S}_2\}]$ [25]. A six-membered central ring in an envelope [1,3-biplanar] conformation was observed. The atoms P(1), C(16), C(25), C(24) and P(2) are approximately coplanar (mean deviation from the plane 0.024), the deviation of Re from the ring being 1.25 . A coplanar arrangement of the naphthalene ring and the metal would necessitate considerable widening of the angles P(1)–C(16)–C(25) ($125.6(9)^\circ$) C16–C25–C24 ($128.7(10)^\circ$) and P(2)–C(24)–C(25) ($126.4(8)^\circ$) and result in increased strain. The out-of-plane distortion of the molecule can be seen from the torsion angles P(1)–C(16)–C(25)–C(24) $0(2)^\circ$ and P(2)–C(24)–C(25)–C(16) $-5(2)^\circ$. The carbonyl groups assume a *fac* geometry with two longer Re–CO bond distances {C(1)–Re(1) $1.979(16)$ and C(3)–Re(1) $1.969(19)$ Å} and a significantly shorter Re–CO bond distance of C(2)–Re(1) $1.909(14)$ Å, *trans* to the terminally coordinated chloride ligand, is comparable to the similar Re–CO bond distances in

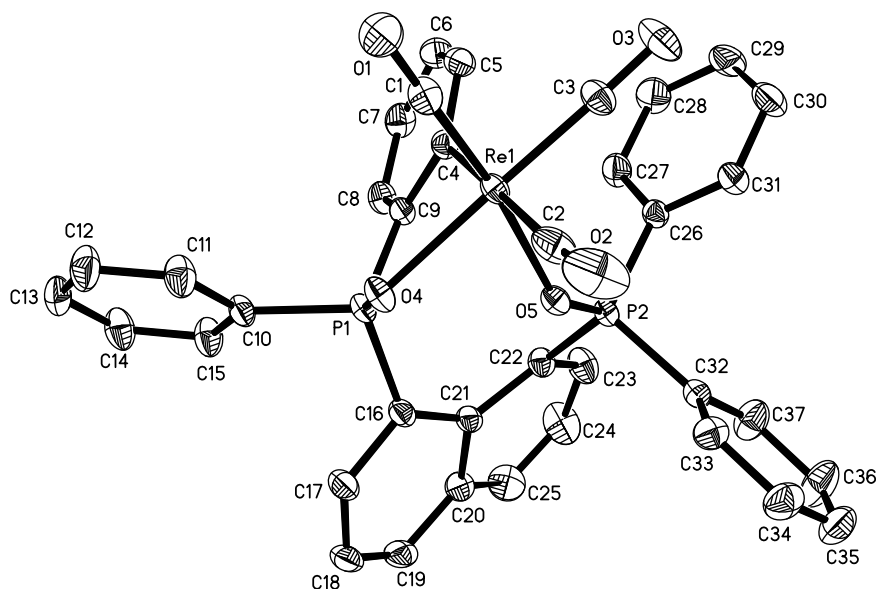


Fig. 2. Molecular structure of *fac*- $[\text{Re}(\text{CO})_3\{\kappa^1:\kappa^1:\eta^1\text{-OPPh}_2\text{C}_{10}\text{H}_6\text{OPPh}(\text{C}_6\text{H}_4)\}]$ (**2**) showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Re(1)–C(1) = $1.876(3)$, Re(1)–C(2) = $1.958(3)$, Re(1)–C(3) = $1.889(3)$, Re(1)–C(4) = $2.169(3)$, Re(1)–O(4) = $2.197(2)$, P(1)–O(4) = $1.520(2)$, P(2)–O(5) = $1.506(2)$, C(1)–Re(1)–C(4) = $98.54(12)$, C(3)–Re(1)–C(4) = $92.90(12)$, C(2)–Re(1)–C(4) = $173.61(12)$, C(2)–Re(1)–O(5) = $91.48(11)$, C(4)–Re(1)–O(5) = $82.15(9)$, C(1)–Re(1)–O(4) = $99.01(11)$, C(2)–Re(1)–O(4) = $98.49(11)$, C(4)–Re(1)–O(4) = $80.29(9)$, O(5)–Re(1)–O(4) = $74.12(8)$.

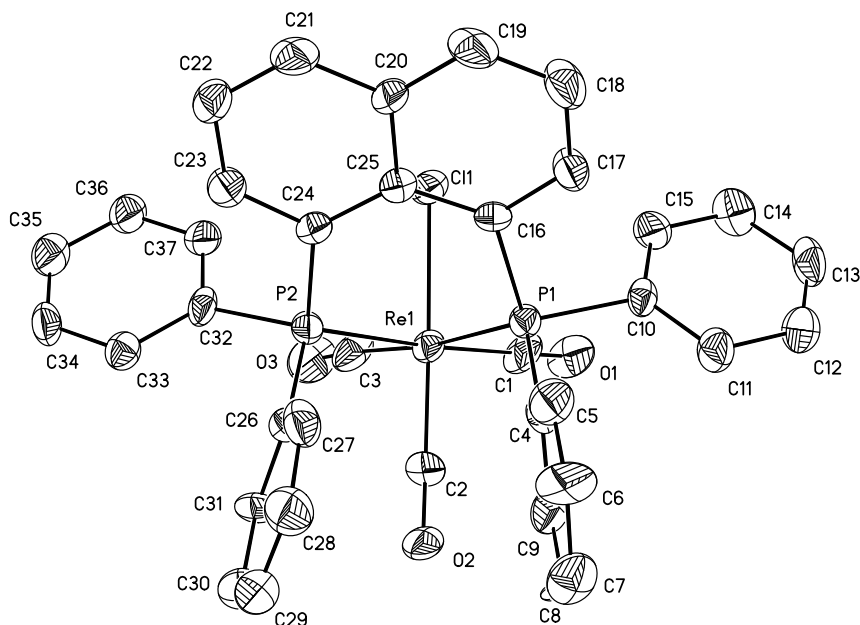


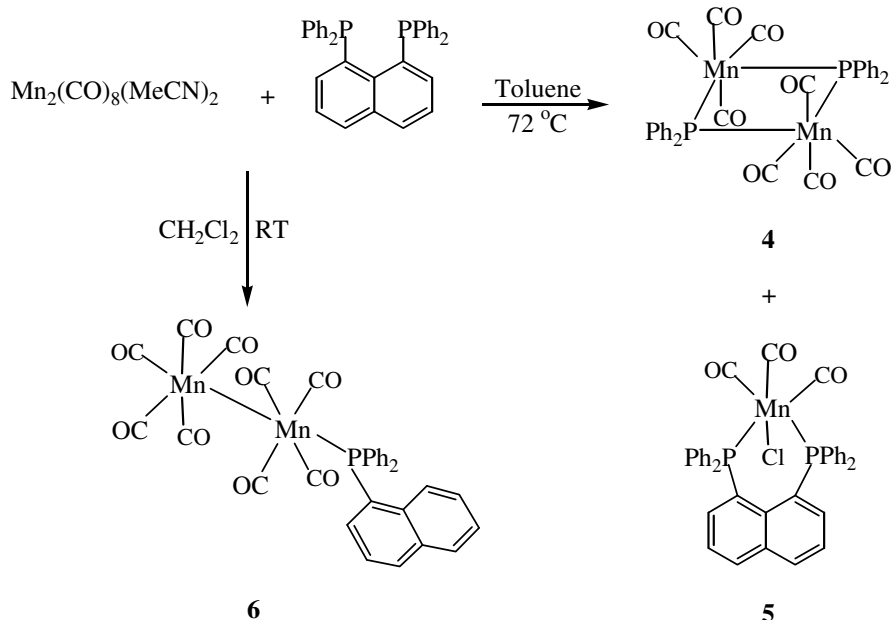
Fig. 3. Molecular structure of *fac*-[ReCl(CO)₃(PPh₂C₁₀H₆PPh₂)] (**3**) showing 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Re(1) = 1.979(16), C(2)–Re(1) = 1.909(14), C(3)–Re(1) = 1.969(19), Cl(1)–Re(1) = 2.495(4), P(1)–Re(1) = 2.459(4), P(2)–Re(1) = 2.446(3), P(2)–Re(1)–P(1) = 82.50(11), P(2)–Re(1)–Cl(1) = 85.76(11), P(1)–Re(1)–Cl(1) = 83.65(12).

fac-[ReCl(CO)₃{κ¹-NC₃H₃N(CH₃)₂}] {1.908(14) Å} [24] and *fac*-[ReCl(CO)₃{κ¹-NC₃H₃S}]] {1.915(8) Å} [25]. The reason for lengthening the other two Re–CO bond distances is probably due the *trans* effect of the two P atoms of the chelating dppn ligand.

The spectroscopic data of **3** are consistent with the solid-state structure. The infrared spectrum displays three bands in the carbonyl stretching region similar to those observed for compounds **1** and **2**. The ¹H NMR spectrum of **3** displays four multiplets at δ 8.05, 7.63, 7.37 and 6.83 and two triplets at δ 7.11 and 6.96 due to the phenyl and naphthyl ring protons of the chelating dppn ligand. The mass spectrum of **3** exhibits a molecular ion peak at *m/z* 802, and fragmentation peaks due to the successive loss of three carbonyl groups.

3.2. Formation of mono- and dimanganese complexes, C–P bond activation in dppn

Reaction of [Mn₂(CO)₈(MeCN)₂] with slight excess of dppn in refluxing toluene, followed by chromatographic separation, lead to the formation of a new compound *fac*-[Mn(Cl)(CO)₃(PPh₂C₁₀H₆PPh₂)] (**5**) along with the known compound [Mn₂(CO)₈(μ-PPh₂)₂] (**4**) in 10 and 23% yields, respectively (Scheme 3). Compound **4** was previously characterized by spectroscopic data and single crystal X-ray diffraction studies [31]. We have characterized **4** by comparing the spectroscopic data with those reported previously, and the new compound **5** by a combination of spectroscopic data and single crystal X-ray diffraction studies.



Scheme 3.

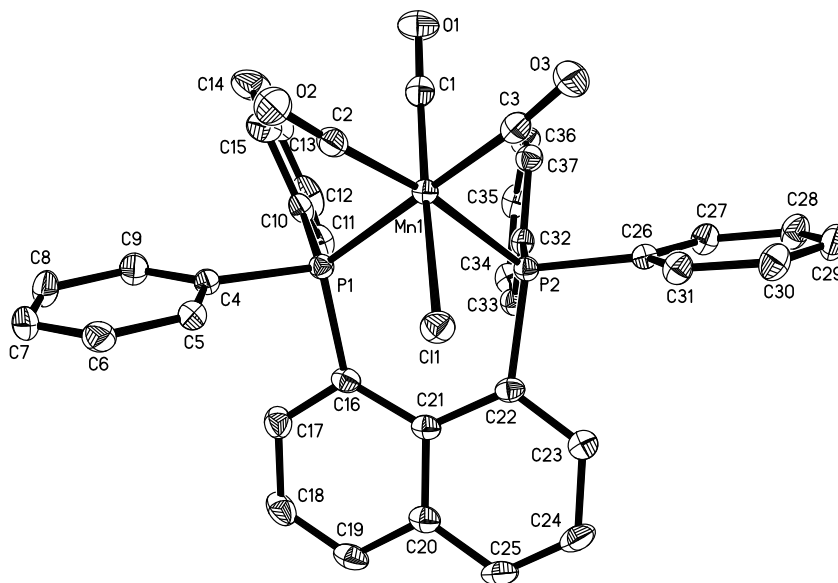


Fig. 4. Molecular structure of *fac*-[MnCl(CO)₃(PPh₂C₁₀H₆PPh₂)] (**5**) showing 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Mn(1)–C(1) = 1.793(2), Mn(1)–C(3) = 1.825(2), Mn(1)–C(2) = 1.828(2), Mn(1)–P(2) = 2.3256(6), Mn(1)–P(1) = 2.3300(6), Mn(1)–Cl(1) = 2.3978(6), P(2)–Mn(1)–P(1) = 84.01(2), P(2)–Mn(1)–Cl(1) = 86.20(2), P(1)–Mn(1)–Cl(1) = 92.22(2).

The crystal structure of **5** is isomorphous with that of **3**, and the molecular structure of one of the two molecules in the asymmetric unit is shown in Fig. 4 with selected bond distances and angles in the caption. The coordination geometry at the Mn atom is closely similar to that already discussed for compound **3**. For example, the distortion from octahedral coordination geometry at the metal is evident from the P–Mn–P angle, 82.50(11)°, comparable with the P–Re–P angle {81.267(13)°} in **3**. The distortions of the ligands discussed for **3** are also manifest in **5**. The only truly significant differences between the two structures are in the bonds to the ligating

atoms. The carbonyl groups exhibit two longer Mn–CO bond distances {Mn(1)–C(3) 1.825(2) and Mn(1)–C(2) 1.828(2) Å} and one shorter Mn–CO bond distance of Mn(1)–C(1) 1.793(2) Å, *trans* to the terminally coordinated chloride ligand. These distances are consistently shorter than those observed in **3** by ca. 0.11–0.15 Å. A similar systematic shortening is seen in the bond lengths to the ligating chlorine and phosphorus atoms. These differences are consistent with the well known covalent radii for manganese and rhenium.

The spectroscopic data for **5** are consistent with the solid-state structure. The infrared spectrum shows three bands in the

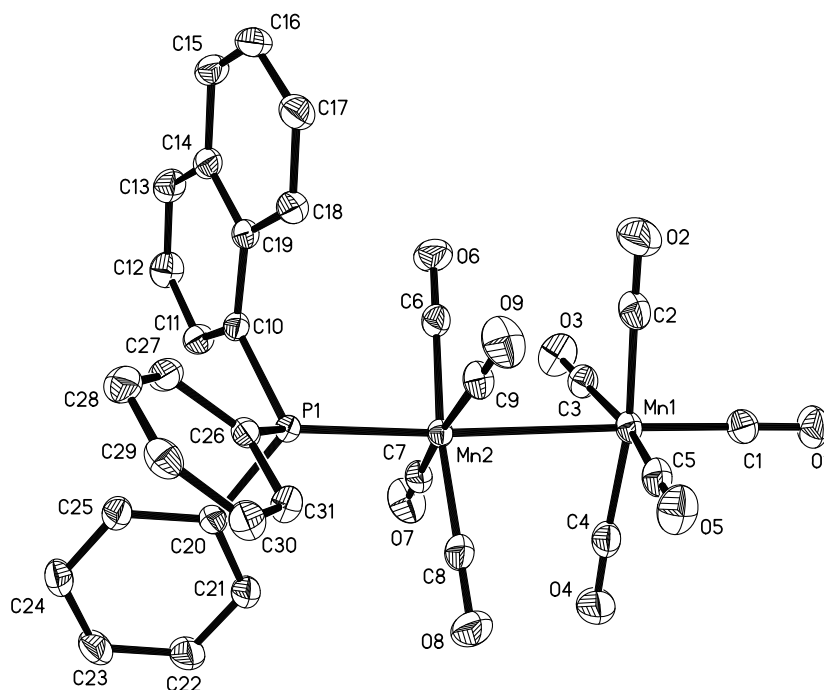


Fig. 5. Molecular structure of [Mn₂(CO)₉(κ¹-PPh₂(C₁₀H₇))] (**6**) showing 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Mn(1)–C(1) = 1.8107(16), Mn(1)–C(3) = 1.8472(17), Mn(1)–Mn(2) = 2.9124(3), Mn(2)–P(1) = 2.2706(4), Mn(2)–C(7) = 1.8349(16), Mn(2)–C(8) = 1.8429(16), P(1)–Mn(2)–Mn(1) = 176.625(13), C(1)–Mn(1)–Mn(2) = 178.63(5), C(3)–Mn(1)–Mn(2) = 85.10(5).

carbonyl stretching region similar to those observed for compounds **1–3**. The ^1H NMR spectrum of **5** displays six well separated multiplets centered at δ 8.04, 7.79, 7.39, 7.11, 6.95 and 6.86 in a relative intensity of 2:3:10:3:4:4 due to the phenyl and naphthyl ring protons of the dppn ligand. As expected the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibits a singlet at δ 49.5. The mass spectrum of **5** exhibits molecular ion peak at m/z 670 and peaks due to the successive loss of the carbonyl groups.

Treatment of $[\text{Mn}_2(\text{CO})_8(\text{MeCN})_2]$ with a slight excess of dppn in CH_2Cl_2 , followed by chromatographic separation, lead to the formation of compound $[\text{Mn}_2(\text{CO})_9\{\kappa^1\text{-PPh}_2(\text{C}_{10}\text{H}_7)\}]$ (**6**) in 12% yield (Scheme 3). Compound **6** has been characterized by a combination of IR, NMR, mass spectral data, elemental analysis and single crystal X-ray diffraction studies.

The molecular structure of **6** is shown in Fig. 5 and selected bond distances and angles are listed in the caption. The molecule contains a Mn–Mn bond with a length of 2.9124(3) Å, comparable to that found in $[\text{Mn}_2(\text{CO})_{10}]$ {2.9030(6) Å} [32]. The overall structure of **6** is similar to that of $[\text{Mn}_2(\text{CO})_{10}]$, in which two square-pyramidal MnL_5 groups are joined by a Mn–Mn single bond with the equatorial ligands adopting a staggered arrangement on the two metal atoms. The diphenylnaphthylphosphine ligand occupies one of the axial coordination sites and is formed by the facile P–C bond cleavage of the initially coordinated κ^1 -dppn ligand and addition of H at the position vacated by phosphorus. The fate of this PPh_2 fragment remains unknown. Such a facile bond cleavage was previously observed in the reaction of 1,8-bis(diphenylphosphino)naphthalene (dppn) with $[\text{Ru}_3(\text{CO})_{12}]$ [12]. We were unable to avoid the ready loss of the PPh_2 fragment from dppn, rather than the further substitution for CO in $[\text{Mn}_2(\text{CO})_9\{\kappa^1\text{-PPh}_2(\text{C}_{10}\text{H}_6)\text{PPh}_2\}]$. The Mn–P bond length in **6** is 2.2706(4) Å, which is comparable to the average Mn–P bond distance of 2.23 Å in $[\text{Mn}_2(\text{CO})_8(\text{PMePh}_2)_2]$ [33]. Most probably, the mono-substituted compound **6** results from the $[\text{Mn}_2(\text{CO})_9(\text{MeCN})]$ impurity in $[\text{Mn}_2(\text{CO})_8(\text{MeCN})_2]$. We have demonstrated this by a individual synthesis of **6** from the room temperature reaction of $[\text{Mn}_2(\text{CO})_9(\text{MeCN})]$ with dppn.

The spectroscopic data for **6** are consistent with the solid-state structure. The infrared spectrum displays four absorption bands in the carbonyl stretching region similar to those observed for compounds of the type of $\alpha\text{-}[\text{Mn}_2(\text{CO})_9\text{L}]$ [34]. The ^1H NMR spectrum of **6** displays multiplets at δ 7.94–7.83 and 7.62–7.42 due to the phenyl and naphthyl ring protons of the diphenylnaphthylphosphine ligand. The mass spectrum of **6** exhibits molecular ion peak at m/z 674, corresponding to its formulation and ions due to the successive loss of nine carbonyl groups.

4. Conclusions

The reactions of the labile complexes $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ and $[\text{Mn}_2(\text{CO})_8(\text{MeCN})_2]$ with the diphosphine ligand dppn have been investigated. This study demonstrates that the reactions of the sterically demanding dppn ligand with dinuclear rhenium and manganese carbonyl complexes result mainly in C–H and C–P bond-cleavage reactions and chelation to one metal center. Three new mononuclear rhenium complexes bearing terminally coordinated PPh_2H and chelating $\text{PPh}_2\text{C}_{10}\text{H}_6$ coordinated in the $\kappa^1:\eta^1$ -mode (compound **1**), cyclometalated (dppndioxide-H) ligand coordinated in the $\kappa^1:\kappa^1:\eta^1$ -mode (compound **2**) and chelating dppn (compound **3**) derived from the reaction of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with dppn have been structurally characterized. The $\text{PPh}_2\text{C}_{10}\text{H}_6$ ligand results from cleavage of one P–C₁₀ bond of dppn with loss of a PPh_2 group, which combines with the H of the oxidatively added dppn-dioxide ligand in **2** and forms the terminally coordinated PPh_2H in **1**. These results contrast with those obtained from the similar reaction with $[\text{Mn}_2(\text{CO})_8(\text{MeCN})_2]$, which afforded

the previously reported dinuclear compound $[\text{Mn}_2(\text{CO})_8(\mu\text{-PPh}_2)_2]$ **4**, formed by C–P bond cleavage of the ligand, and the new compound **5**, the manganese analog of **3**, containing an unaltered chelating dppn and a terminal Cl ligand. We have not been able to isolate any complexes in which the C10 fragment interacts with metal carbonyl moieties. $[\text{Mn}_2(\text{CO})_8(\text{MeCN})_2]$ also reacts with dppn at room temperature affording compound **6** by a facile cleavage of one P–C₁₀ bond and the loss of PPh_2 group.

Supplementary material

CCDC 621647, 672288, 672410, 672289 and 672290 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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