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Iron carbonyl complexes bearing phenazine and acridine ligands: X-ray structures of \( \text{Fe(CO)}_3(\eta^4\text{-C}_{12}\text{H}_8\text{N}_2) \), \( \text{Fe(CO)}_2\{\text{P(OMe)}_3\}(\eta^4\text{-C}_{12}\text{H}_8\text{N}_2) \), \( \text{Fe(CO)}_2(\text{PPh}_3)(\eta^4\text{-C}_{13}\text{H}_9\text{N}) \), and \( \text{Fe(CO)}_2(\kappa^1\text{dppm})(\eta^4\text{-C}_{12}\text{H}_8\text{N}_2) \)

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Abstract

Reactions of $\text{Fe}_3(\text{CO})_{12}$ with the heterocycles phenazine and acridine in refluxing benzene afforded the mononuclear complexes $\text{Fe}(\text{CO})_3(\eta^4-\text{C}_{12}\text{H}_8\text{N}_2)$ (1a) and $\text{Fe}(\text{CO})_3(\eta^4-\text{C}_{13}\text{H}_9\text{N})$ (1b), respectively. Treatment of 1a with $\text{P(OMe)}_3$ and PPh$_3$ in the presence of Me$_3$NO at room temperature yielded the carbonyl substitution products $\text{Fe}(\text{CO})_2\{\text{P(OMe)}_3\}(\eta^4-\text{C}_{12}\text{H}_8\text{N}_2)$ (2a) and $\text{Fe}(\text{CO})_2(\text{PPh}_3)(\eta^4-\text{C}_{13}\text{H}_9\text{N})$ (3a), respectively. Similar reactions of 1b yielded $\text{Fe}(\text{CO})_2\{\text{P(OMe)}_3\}(\eta^4-\text{C}_{13}\text{H}_9\text{N})$ (2b) and $\text{Fe}(\text{CO})_2(\text{PPh}_3)(\eta^4-\text{C}_{13}\text{H}_9\text{N})$ (3b). Treatment of 1a with the diphosphines dppm and dppf under similar conditions afforded the mononuclear compounds $\text{Fe}(\text{CO})_2(\kappa^1\text{-dppm})(\eta^4-\text{C}_{12}\text{H}_8\text{N}_2)$ (4a) and $\text{Fe}(\text{CO})_2(\kappa^1\text{-dppf})(\eta^4-\text{C}_{12}\text{H}_8\text{N}_2)$ (4b). Compounds 1a, 2a, 3b, and 4a have been structurally characterized by X-ray crystallography. The ancillary phenazine and acridine ligands in these products adopt an $\eta^4$-coordination mode by using only the peripheral carbon atoms in one of the carbocyclic rings. Given the rarity of this coordination mode in metal carbonyl complexes, we have performed electronic structure calculations on 1a and these data are discussed relative to the solid-state structure.

Keywords: Iron carbonyl; Phenazine; Acridine; Phosphines; X-ray structure; DFT calculations

1. Introduction

Phenazine, a bisannulated derivative of pyrazine, is a planar $N$-heterocyclic ligand whose biological and spectral properties have been extensively studied in the fields of chemistry and biology.$^{1,2,3,4,5,6,7,8}$ Although similar to the parent heterocycle, pyrazine, with respect to its $N$-based coordination chemistry, it has different electronic and steric properties, which in turn give rise to ligand coordination modes and unique structural motifs for those compounds that possess an ancillary phenazine. Phenazine possesses idealized $C_{2h}$ symmetry similar to pyrazine, but the presence of the fused benzene rings at the [2,3-b] and [5,6-e] pyrazine junctions imparts additional steric bulk to phenazine related to the parent heterocycle and the monoannulated derivative quinoxaline. As an ancillary ligand, phenazine is known to exhibit terminal$^9$ and bridging$^{10}$ coordination modes, as well as functioning as an electron donor in intermolecular arrays by directing the formation of columnar stacks through $\pi-\pi$ interactions.$^{11}$ Acridine contains only one nitrogen atom and its structural properties and reactivity often mimic that of phenazine.
The ligand substitution chemistry displayed by the trimetal clusters $M_3(CO)_{12-n}(MeCN)_n$ (where $M = Fe$, Ru, Os; $n = 0, 1, 2$) typically reveals great diversity in reactivity and structural outcome between the Fe$_3$ versus the Ru$_3$ and Os$_3$ analogs. Of the numerous substrates investigated in such substitution reactions, nitrogen-containing heterocycles have received considerable attention. The driving force behind these studies is attributed to industrial demands for selective and catalytic transformations of commonplace heterocyclic substrates to high-value commodity chemicals. This interest is further supplemented by the increased importance for industrial hydrodenitriﬁcation of crude oil feedstocks that are employed in the production of higher value petroleum distillates.

While the reactivity of the triruthenium and triosmium clusters $M_3(CO)_{12-n}(MeCN)_n$ with the nitrogen heterocycles pyridine, pyrazole, pyrimidine, quinoxaline, and quinoline has been extensively been investigated, few studies have hitherto been published involving the heterocycle phenazine. Cabeza et al. recently reported that the reaction of Ru$_3(CO)_{12}$ with phenazine in refluxing THF led to the formation of tri-, tetra- and hexanuclear clusters Ru$_3(CO)_9(\mu_3-\{C_6H_4)(C_6H_3)N_2\})(\mu-H)$, Ru$_4(CO)_{10}(\mu-CO)(\mu_4-\{C_6H_4)(C_6H_3)N_2H\}$ and Ru$_6(CO)_{12}(\mu-CO)(\mu_5-\{C_6H_4)(C_6H_3)N_2H\}$ (Scheme 1).

![Scheme 1]

More recently, we reported the isolation and structural characterization of the face-capped monohydride Os$_3(CO)_{9}(\mu_3-\eta^2-C_{12}H_7N_2)(\mu-H)$ and electron-precise dihydride Os$_3(CO)_{9}(\mu_3-\eta^2-C_{12}H_6N_2)(\mu-H)_2$ clusters from the reaction of Os$_3(CO)_{12}$ with phenazine in refluxing xylene (Scheme 2).
In order to complete the study of phenazine reactivity with the Group 8 trimetallic clusters, we have investigated the reaction of Fe₃(CO)₁₂ with phenazine. Herein, we report our results on the mononuclear iron compound Fe(CO)₃(η⁴-C₁₂H₈N₂) (1a), which was isolated from the thermolysis of Fe₃(CO)₁₂ in the presence of phenazine. Also reported is the reactivity of acridine with Fe₃(CO)₁₂ under analogous conditions, which furnishes Fe(CO)₃(η⁴-C₁₃H₉N) (1b). Our data reveal that the two heterocyclic ligands adopt a different coordination mode in the case of iron compared to the products found in the related reactions using ruthenium and osmium carbonyl cluster complexes.

2. Experimental

2.1. General procedures

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Reagent-grade solvents were dried using appropriate drying agents and distilled prior to use by standard methods. Fe₃(CO)₁₂ was prepared according to the published procedure.²⁶ Phenazine and acridine were purchased from Sigma-Aldrich and used without further purification. Me₃NO·2H₂O was dried by azeotropic distillation using benzene with Dean–Stark distillation equipment. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer, and the ¹H and ¹³C NMR spectra were recorded on a Varian Unity 500 NMR spectrometer. The spectral assignments for 1a were ascertained through a combination of 2D NMR experiments, including ¹H COSY, HMQC, and HMBC techniques. All chemical shifts are reported in δ units and are referenced to the residual protons of the deuterated solvents (¹H and ¹³C) and external 85% H₃PO₄ (³¹P) as appropriate. Elemental analyses were performed by the Microanalytical Laboratories of the Wazed Miah Science Research Centre at Jahangirnagar University. Product separations were performed by TLC in air on 0.5 mm silica gel (GF₂₅₄-type 60, E. Merck, Germany) glass plates.
2.2. Reaction of Fe$_3$(CO)$_{12}$ with phenazine

A benzene solution (25 mL) containing Fe$_3$(CO)$_{12}$ (0.20 g, 0.40 mmol) and phenazine (71 mg, 0.39 mmol) was heated to reflux for 3 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH$_2$Cl$_2$ (2:3, v/v) developed four bands. The slowest moving band afforded Fe(CO)$_3$(η$^4$-C$_{12}$N$_2$H$_8$) (1a) (0.18 g, 47%) as orange crystals after recrystallization from dichloromethane/hexane at 4 °C. The first and second bands were too small for complete characterization, while the third band afforded unreacted phenazine. Spectral data for 1a: IR (νCO, CH$_2$Cl$_2$): 2064 vs, 2005 vs, 1997 sh cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$): δ 3.87 (AA', diene, J = 5.4, 3.5 Hz, 2H), 6.53 (XX', diene, J = 5.4, 3.5 Hz, 2H), 7.38 (AA', aryl, J = 6.5, 3.0 Hz, 2H), 7.51 (BB', J = 6.5, 3.0 Hz, 2H). $^{13}$C NMR (CD$_2$Cl$_2$): δ 62.14 (CH), 88.03 (CH), 127.55 (CH), 128.18 (CH), 139.46 (C), 156.98 (C), 207.25 (Fe-CO). Anal. Calcd. for C$_{15}$H$_8$FeN$_2$O$_3$: C, 56.29; H, 2.52; N, 8.75. Found: C, 56.55; H, 2.72; N, 8.83%.

A similar reaction between Fe$_2$(CO)$_9$ (50 mg, 0.14 mmol) and phenazine (25 mg, 0.14 mmol), followed by similar chromatographic separation, afforded 1a (18 mg, 20%), while use of Fe(CO)$_5$ (50 mg, 0.26 mmol) as the iron precursor (46 mg, 0.26 mmol) also furnished 1a (15 mg, 18%).

2.3 Reaction of Fe$_3$(CO)$_{12}$ with acridine

A benzene solution (25 mL) of Fe$_3$(CO)$_{12}$ (0.10 g, 0.20 mmol) and acridine (0.11 g, 0.59 mmol) was heated to reflux for 1.5 h and then allowed to cool to room temperature. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/acetone (4:1, v/v) developed four bands. The third band gave Fe(CO)$_3$(η$^4$-C$_{13}$H$_9$N) (1b) (66 mg, 35%) as orange crystals after recrystallization from hexane/CH$_2$Cl$_2$ at 4 °C. The first and the fourth bands corresponded to unreacted Fe$_3$(CO)$_{12}$ and acridine, respectively. The second band was too small for complete characterization. Spectral data for 1b: IR (νCO, CH$_2$Cl$_2$): 2057 vs, 1995 s, 1983 sh cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 7.65 (d, 1H, J = 5.5 Hz), 7.41 (d, 2H, J = 7.2 Hz), 7.28 (s, 1H), 7.14 (s, 1H), 6.56 (s, 1H), 6.40 (s, 1H), 3.88 (s, 1H), 3.77 (s, 1H). Anal. Calcd. for C$_{16}$H$_9$FeNO$_3$: C, 60.22; H, 2.84; N, 4.39. Found: C, 60.42; H, 3.05; N, 4.58%.

2.4. Reaction of 1a with P(OMe)$_3$
To a dichloromethane solution (20 mL) of 1 (20 mg, 0.06 mmol) and P(OMe)$_3$ (15 μL, 0.12 mmol) was added dropwise a solution of Me$_3$NO (5 mg, 0.01 mmol) in the same solvent (10 mL) and the solution was stirred at room temperature for 2h. The solution was then filtered through a short silica column (4 cm), followed by solvent removal under reduced pressure. The resulting residue was purified by chromatography over silica gel using cyclohexane/CH$_2$Cl$_2$ (1:9, v/v) as the eluent. Of the two developed two bands, the faster moving band corresponded to unconsumed 1a (trace), while the slower moving bond yielded Fe(CO)$_2$[P(OMe)$_3$]($\eta^4$-C$_{12}$H$_8$N$_2$) (2a) (23 mg, 88%). The analytical sample of 2a was isolated as red crystals after recrystallization from hexane/CH$_2$Cl$_2$ at 4 °C. Spectral data for 2a: IR (vCO, CH$_2$Cl$_2$): 2008 vs, 1954 vs cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 7.47 (m, 2H), 7.31 (m, 2H), 6.23 (m, 2H), 3.62 (m, 2H), 3.58 (d, $J = 15.0$ Hz, 9H). $^{31}$P{$^1$H}NMR (CDCl$_3$): δ 174.6 (s).

2.5. Reaction of 1b with P(OMe)$_3$

A similar reaction between 1b (20 mg, 0.06 mmol) and P(OMe)$_3$ (15 μL, 0.12 mmol) in the presence of Me$_3$NO (10 mg, 0.01 mmol) yielded Fe(CO)$_2$[P(OMe)$_3$]($\eta^4$-C$_{13}$H$_9$N) (2b) (21 mg, 80%) as red crystals after recrystallization from hexane/CH$_2$Cl$_2$ at 4 °C. Spectral data for 2b: IR (vCO, CH$_2$Cl$_2$): 1999 (vs), 1943 (vs) cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 7.47 (m, 2H), 7.31 (m, 2H), 6.23 (m, 2H), 3.62 (m, 2H), 3.58 (d, $J = 15.0$ Hz, 9H). $^{31}$P{$^1$H}NMR (CDCl$_3$): δ 174.6 (s). Anal. Calcd. for C$_{18}$H$_{18}$FeN$_2$O$_2$P: C, 52.08; H, 4.37; N, 3.37. Found: C, 52.28; H, 4.55; N, 3.48%.

2.6. Reaction of 1a with PPh$_3$

To a dichloromethane solution (20 ml) of 1a (40 mg, 0.13 mmol) and triphenylphosphine (33 mg, 0.126 mmol) was added dropwise a CH$_2$Cl$_2$ solution containing Me$_3$NO (10 mg, 0.013 mmol), followed by stirring at room temperature for 2h. Filtration of the crude reaction mixture through a short silica column (4 cm), followed by solvent removal, afforded the crude product. Chromatographic purification using cyclohexane/dichloromethane (2:3, v/v) developed four bands, of which the first band was confirmed as unreacted triphenylphosphate. The second band was too small for complete characterization and the third band was phenazine (trace). The fourth band gave the desired product [Fe(CO)$_2$(PPh$_3$)($\eta^4$-C$_{12}$H$_8$N$_2$)] (3a) (66 mg, 95%) as red crystals after recrystallization from hexane/CH$_2$Cl$_2$.
dichloromethane/hexane at 4 °C. Spectral data for 3a: IR (νCO, CH₂Cl₂): 1997 (vs), 1943 (vs) cm⁻¹. ¹H NMR (CDCl₃): δ 7.44 (m, 17H), 7.39 (m, 2H), 5.98 (m, 2H), 3.30 (m, 2H). ³¹P{¹H} NMR (CDCl₃): δ 67.0 (s). Anal. Calcd. for C₃₂FeH₂₃N₂O₂P: C, 69.30; H, 4.18; N, 5.05. Found: C, 69.60; H, 4.40; N, 5.15%.

2.7. Reaction of 1b with PPh₃

A similar reaction between 1b (26 mg, 0.08 mmol) and triphenylphosphine (21 mg, 0.08 mmol) in the presence of Me₃NO (6 mg, 0.08 mmol) was conducted and Fe(CO)₂(PPh₃)(η⁴-C₁₃H₉N) (3b) (40 mg, 88%) was isolated as red crystals after recrystallization from dichloromethane/hexane at 4 °C. Spectral data for 3b: IR (νCO, CH₂Cl₂): 1988 (vs), 1933 (vs) cm⁻¹. ¹H NMR (CDCl₃): δ 7.60 (d, J = 8.0 Hz, 1H), 7.43 (m, 15H), 7.33 (t, J = 8.0 Hz, 2H), 7.19 (t, J = 8.0 Hz, 1H), 6.84 (s, 1H), 6.06 (s, 1H), 5.90 (s, 1H), 3.38 (s, 1H), 2.98 (s, 1H). ³¹P{¹H} NMR (CDCl₃): δ 66.6 (s). Anal. Calcd. for C₃₃H₂₄FeNO₂P: C, 71.62; H, 4.37; N, 2.53. Found: C, 71.79; H, 4.46; N, 5.56%.

2.9. Reaction of 1a with dppm

To a dichloromethane solution of 1a (20 mg, 0.06 mmol) and dppm (24 mg, 0.06 mmol) was added dropwise a solution of Me₃NO (5 mg, 0.006 mmol) in the same solvent (10 mL) and stirring continued for 2 h at room temperature. The solution was filtered through a short silica column (4 cm), after which time the solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH₂Cl₂ (1:9, v/v) developed two bands. The faster moving band afforded Fe(CO)₂(k¹-dppm)(η⁴-C₁₂H₈N₂) (4a) (18 mg, 40%) and slower moving band was isolated in an insufficient amount for spectroscopic characterization. Spectral data for 4a: IR (νCO, CH₂Cl₂): 1996 (vs), 1942 (vs) cm⁻¹. ¹H NMR(CDCl₃): δ 7.36 (m, 6H), 7.28 (m, 18H), 6.04 (m, 4H), 3.23 (m, 1H), 3.04 (m, 1H). ³¹P{¹H} NMR (CDCl₃): δ 57.5 (d, J = 76.0 Hz, 1P), -24.2 (d, J = 76.0 Hz, 1P). Anal. Calcd. for C₃₉H₃₀FeN₂O₂P₂: C, 69.25; H, 4.47; N, 4.14. Found: C, 69.42; H, 4.62; N, 4.32%.

2.8. Reaction of 1a with dppf

To a dichloromethane solution (20 mL) of 1a (20 mg, 0.06 mmol) and dppf (35 mg, 0.06 mmol) was added dropwise a CH₂Cl₂ solution (10 mL) of Me₃NO (5 mg, 0.06 mmol) over a period of 30 min and stirred for an additional 5 h at room temperature. The reaction mixture was then filtered through a short silica column (4 cm). The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with
cyclohexane/dichloromethane (3:7, v/v) developed four bands. The first and second bands were unreacted dppf and phenazine, respectively. The third gave Fe(CO)\(_2\)(κ\(^1\)-dppf)(η\(^4\)-C\(_{12}\)H\(_8\)N\(_2\)) (5a) (21 mg, 40%) while the fourth band afforded a trace amount of material insufficient for characterization. Spectral data for 5a: IR (vCO, CH\(_2\)Cl\(_2\)): 1994(vs), 1941(vs) cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)): δ 7.43 (m, 20H), 7.23 (m, 4H), 5.91 (m, 2H), 4.45 (m, 2H), 4.22 (m, 2H), 3.86 (m, 2H), 3.70 (m, 2H), 3.06 (m, 2H). \(^{31}\)P{\(^1\)H} NMR (CDCl\(_3\)): δ 61.0 (s, 1P) -18.1 (s, 1P). Anal. Calcd. for C\(_{48}\)H\(_{36}\)Fe\(_2\)N\(_2\)O\(_2\)P\(_2\): C, 68.11; H, 4.29; N, 3.31. Found: C, 68.31; H, 4.42; N, 3.46\%.

2.9. X-ray crystallography

2.10. Computational details and modeling

The DFT calculations on Fe(CO)\(_3\)(η\(^4\)-C\(_{12}\)H\(_8\)N\(_2\)) (species A) were carried out with the Gaussian 09 package of programs,\(^{27}\) using the B3LYP hybrid functional. This functional is comprised of Becke's three-parameter hybrid exchange functional (B3)\(^{28}\) and the correlation functional of Lee, Yang, and Parr (LYP).\(^{29}\) The iron atom was described with the Stuttgart-Dresden effective core potential and SDD basis set,\(^{30}\) and the 6-31G(d') basis set\(^{31}\) was employed for all remaining atoms.

The reported geometry for A was were fully optimized and the analytical second derivatives were evaluated, confirming that the geometry was an energy minimum (no negative eigenvalues). Unscaled vibrational frequencies were used to make zero-point and thermal corrections to the electronic energies. The computed harmonic frequencies for the carbonyl stretching bands have been scaled using a scaling factor of 0.965. The natural charges and Wiberg indices were computed using Weinhold’s natural bond orbital (NBO) program.\(^{32,33}\) The geometry-optimized structures have been drawn with the JIMP2 molecular visualization and manipulation program.\(^{34}\)

3. Results and discussion

3.1. Reactions of Fe\(_3\)(CO)\(_{12}\) with phenazine and acridine

Treatment of Fe\(_3\)(CO)\(_{12}\) with phenazine and acridine in refluxing benzene afforded the mononuclear complexes Fe(CO)\(_3\)(η\(^4\)-C\(_{12}\)H\(_8\)N\(_2\)) (1a) (47\% yield) and Fe(CO)\(_3\)(η\(^4\)-C\(_{13}\)H\(_9\)N) (1b) (35\% yield), respectively, which were isolated as yellow crystals after chromatographic workup. Both new compounds 1a and 1b have been characterized by a combination of
elemental analysis, IR, and $^1$H NMR spectroscopy; the solid-structure of 1a was also determined by single crystal X-ray diffraction analysis.

![Scheme 3](image)

The ORTEP drawing of the molecular structure of 1a is depicted in Fig. 1 (top) and selected bond distances and angles are reported in the figure caption. The molecule contains one iron atom whose coordination sphere consists of three carbonyl ligands and an $\eta^4$-C$_{12}$H$_8$N$_2$ ligand. The $\eta^4$ coordination of the phenazine in 1a represents a rare bonding mode for this ligand. While $\eta^4$-phenazine ligands have been structurally demonstrated by Parkin et al.\textsuperscript{35} in a series of molybdenum compounds and by Yang et al.\textsuperscript{36} for one nickel diamine complex, no entries of mononuclear iron compounds exist in the Cambridge Structural Database (CSD version 5.36, November 2014). To our knowledge, the iron compounds reported here represent the first such examples that reveal the $\eta^4$ coordination of phenazine and acridine ligands. 1a contains 18e and is electronically saturated, with the CO groups and diene moiety contributing a total of 6e and 4e, respectively to the total electron count. The orientation of the ancillary CO groups relative to the coordinated phenazine is not unlike that found in structurally characterized iron and ruthenium M(CO)$_3$($\eta^4$-diene) compounds.\textsuperscript{37} The theoretical basis for the preferred disposition of the Fe,Ru(CO)$_3$ rotor relative the polyene framework has been previously addressed.\textsuperscript{38} The mean Fe-C bond distance of 2.056 Å for the outer carbon atoms associated with the diene moiety [Fe(1)-C(5) and Fe(1)-C(6)] is 0.101 Å shorter than the mean Fe-C distance for the inner Fe-C(diene) vectors [Fe(1)-C(4) and Fe(1)-C(7)]. Another important aspect of the structure is, as expected, the carbon-carbon bond distances of the coordinated benzo ring [C(4)-C(5) 1.430(3), C(6)-C(7) 1.425(3), Å] are longer than those of the uncoordinated benzo ring [C(10)-C(11) 1.403(3), C(11)-C(12) 1.414(3), C(12)-C(13) 1.377(3), C(13)-C(14) 1.393(3), C(14)-C(15) 1.376(3), C(15)-C(10) 1.412(3) Å]. The C-N bond distances involving coordinated benzo group [N(1)-C(8) 1.308(2), N(2)-C(9) 1.312(2) Å] are shorter than those of the uncoordinated benzo ring [N(1)-C(11) 1.386(2), N(2)-C(10) 1.394(2) Å]. The DFT
optimized structure of A is depicted below that of 1a in Figure 1, and an excellent correspondence exists between the two structures. The Wiberg bond indices (WBI) computed for the heterocyclic scaffold (shown below) parallel the experimentally determined bond lengths and underscore the bond length alterations depicted by the resonance contributor of 1a in Scheme 3.

The solution spectroscopic data of 1a are in complete agreement with the solid-state structure. The infrared spectrum of 1a recorded in CH₂Cl₂ reveals three terminal ν(CO) bands at 2065, 2005, and 1997 cm⁻¹, of which the highest energy band corresponds to the symmetric stretching mode for the three vibrationally coupled carbonyl groups. The remaining two ν(CO) bands represent different combinations of antisymmetric stretches involving the carbonyl groups. The nature of these assignments was ascertained by normal mode analysis of the frequency data from the DFT-optimized structure. The ¹H NMR spectrum of 1a (recorded in CD₂Cl₂) shows two different sets of symmetrical spin systems for the eight hydrogens. The diene moiety appears as an AAXX' system with multiplets centered at δ 3.87 and 6.53, while the remaining four hydrogens on the iron-free aryl ring appear as an AA'BB' spin system. The specific assignments in these spin systems were verified by ¹H COSY measurements and the coupling constants were established by spectral simulation using the available program gNMR. The ¹³C NMR spectrum reveals eight ¹³C resonances, of which the seven that appear from δ 62.14 to 156.98 belong to the phenazine ligand that possesses idealized C₂ symmetry. Rapid tripodal rotation of three CO groups leads to a time-averaged resonance at δ 207.25. The ¹³C spectral assignments were determined by a combination of HMQC and HMBC experiments, and the below picture shows the specific ¹H (black) and ¹³C (red) NMR assignments for 1a. The IR and ¹H spectral data recorded for 1b were similar in nature and are summarized in the experimental section.
3.2. Reactions of 1a and 1b with monodentate phosphines

The ligand substitution reactivity of 1a and 1b was next explored as a check of the lability of the coordinated heterocycle in the presence of P-donors. Trimethylamine N-oxide initiated reactions of 1a with trimethylphosphite and triphenylphosphine at room temperature afforded the mono-substituted products Fe(CO)$_2$[P(OMe)$_3$](η$^4$-C$_{12}$H$_8$N$_2$) (2a) and Fe(CO)$_3$(PPh$_3$)(η$^4$-C$_{12}$H$_8$N$_2$) (3a) as red crystals in 88 and 95% yields, respectively. The reaction of 1b with P(OMe)$_3$ and PPh$_3$ proceeded similarly and furnished Fe(CO)$_2$[P(OMe)$_3$](η$^4$-C$_{13}$H$_9$N) (2b) (80% yield) and Fe(CO)$_3$(PPh$_3$)(η$^4$-C$_{13}$H$_9$N) (3b) (88% yield), respectively. Attempts to substitute a second carbonyl in the initial substitution products 2a,b and 3a,b by either PPh$_3$ or P(OMe)$_3$ in the presence of Me$_3$NO were unsuccessful. In no case was any evidence for the release of the heterocyclic ligand observed.

The data obtained from elemental analyses and IR and NMR spectroscopies corroborate the nature of the products 2a,b and 3b, whose structures are depicted in Scheme 4. Moreover, the solid-state structures of 2a and 3b were also established by X-ray crystallography. The ORTEP drawing of molecular structure of 2a is depicted in Fig. 2, confirming the substitution of a single CO ligand by P(OMe)$_3$ and whose presence is shown to lie underneath the coordinated phenazine ligand. The figure caption lists selected bond distances and angles for 2a. The Fe-C(phenazine) bond distances [Fe(1)-C(7) 2.048(4), Fe(1)-C(8) 2.050(4), Fe(1)-C(6) 2.153(4), Fe(1)-C(9) 2.153(4) Å] are comparable in length to those Fe-C bonds in 1a. The C-C bond lengths in the diene portion of the ligand [C(6)-C(7) 1.428(5), C(7)-C(8) 1.408(5), C(8)-C(9) 1.423(5) Å] are shorter than those carbon-carbon bond lengths associated with the non-coordinated aryl ring [C(6)-C(17) 1.472(5), C(9)-C(10) 1.453(5) Å]. The Fe-P vector exhibits a distance is 2.1647(6) Å, which in turn is intermediate in length compared to the Fe-P bond distance in [Fe(CO)(COMe)(η$^5$-MeC$_5$H$_4$)(PPh$_2$Et)] $\{2.200(2)$ Å $\}$

[40] and [Fe(CO)(η$^1$-C(O)C(Me)=C(Ph)Me)(η$^5$-C$_5$H$_5$)(P(OPh)$_3$)] $\{2.110(1)$ Å $\}$.41
The ORTEP drawing of the molecular structure of 3b is shown in Fig. 3. The molecule is structurally similar to 2a apart from the terminal PPh₃ ligand and the η⁴-acridine ligand. The coordinated PPh₃ adopts one of the two coordination sites at iron that are distal to the heterocycle. The acridine ligand is coordinated to the iron atom in a manner analogous to that of the phenazine ligand in 1a and 2a. The Fe-P bond distance is 2.2277(6) Å and is significantly longer than the Fe-P bond distance in 2a.

The IR spectra of compounds 2a,b and 3a,b display, as expected, two strong carbonyl stretching frequencies (2a: 2008, 1954 cm⁻¹; 2b: 1999, 1943 cm⁻¹; 3a: 1997, 1943 cm⁻¹; 3b: 1988, 1933 cm⁻¹), indicating that the number and arrangement of CO ligands are similar in the four Fe(CO)₂P(η⁴-polyene) species. The shifts of the stretching frequencies to lower wavenumbers going from 1a and 1b to 2a,b and 3a,b are consistent with increased electron density at the iron center from the replacement of a carbonyl ligand with a P-donor ligand. The ³¹P NMR spectrum of each compound displays a single resonance at 8 174.6 (2a), 177.1 (2b), 67.0 (3a), and 66.6 (3b) for the coordinated phosphite/phosphine ligand. The presence
of AA′XX′ and AA′BB′ multiplets in the $^1$H NMR spectrum of 2a are confirmed for the diene and non-coordinated aryl ring protons, and the doublet at $\delta$ 3.58 (9H) is readily ascribed to the methyl protons of the P(OMe)$_3$ ligand. The recorded $^1$H NMR data for 2b are consistent with the proposed structure. Use of PPh$_3$ as a ligand in the substitution reactions with 1a,b afforded products similar to those of 2a,b, and these data are summarized in the experimental section.

3.3. Reactions of 1a with diphosphines

The reactivity of 1a with the diphosphines dppm and dppf were next examined in order to probe the ligand chelation of these diphosphines at the iron center. Heating 1a with dppm at 40 °C in the presence of Me$_3$NO afforded the mononuclear complex Fe(CO)$_2$(κ$^1$-dppm)(η$^4$-C$_{12}$H$_8$N$_2$) (4a) in 40% yield. A comparable product yield was also obtained when the more flexible dppf was employed, furnishing Fe(CO)$_2$(κ$^1$-dppf)(η$^4$-C$_{12}$H$_8$N$_2$) (5a) in 50% yield. Compounds 4a and 5a have been characterized by a combination of elemental analysis, IR, $^1$H and $^{31}$P{$^1$H} NMR spectroscopies, and by single crystal X-ray diffraction analysis in the case of 4a. An ORTEP drawing of the molecular structure of 4a is depicted in Fig. 4 and selected bond distances and angles are reported in the figure caption. The structure of 4a confirms the replacement of a single CO in 1a and the presence of a κ$^1$-coordinated dppm ligand. The Fe-C bond distances to the phenazine ligand [Fe(1)-C(3) = 2.122(4), Fe(1)-C(4) = 2.031(4), Fe(1)-C(5) = 2.038(4), Fe(1)-C(6) = 2.133(4) Å] are slightly shorter than those of the corresponding Fe-C bond distances in 1a. One interesting finding is that among the phenazine carbon atoms coordinated to Fe(1) atom, the two C-C bond lengths are approximately equal [C(3)-C(4) = 1.409(5), C(5)-C(6) = 1.416(5) Å] and slightly longer than that of the other carbon-carbon bond distance [C(4)-C(5) = 1.392(5) Å] define by the diene linkage in 4a. The Fe-P bond distance is 2.2081(12). The remaining bond distances and angles are unremarkable and require no comment.

The spectroscopic data of 4a are fully consistent with the solid-state structure. The IR spectra of compounds 4a and 5a exhibit a similar pattern of CO stretches, indicating that the number and arrangement of CO ligands are similar in both the species. In addition to the characteristic phenyl and phenazine ring proton resonances in the aromatic region, the aliphatic region of $^1$H NMR of 4a displays diastereotopic protons at δ 3.23 and 3.04 (each integrating to 1H) assigned to the methylene protons of the dppm ligand. In each of 4a and 5a, the presence of a dangling diphosphine is easily deduced from the $^{31}$P{$^1$H} NMR spectra,
which exhibit two doublets at $\delta$ 57.0 and -24.0 ($J = 76.0$ Hz) for 4a and two singlets $\delta$ 61.0 and -18.1 for 5a, consistent with the presence of two nonequivalent phosphorus nuclei. The higher field resonance in each species is confidently assigned to the dangling phosphine moiety.

4. Conclusions

A summary of the reactions described in this report is shown in Schemes 3 and 4. The reaction of phenazine and acridine with Fe$_3$(CO)$_{12}$ at 80 °C yielded the mononuclear complexes Fe(CO)$_3$($\eta^4$-C$_{12}$H$_8$N$_2$) (1a) and Fe(CO)$_3$($\eta^4$-C$_{13}$H$_9$N) (1b) as the sole isolable products. Four new substituted derivatives Fe(CO)$_2$P($\eta^4$-heterocycle) [where P = P(OMe)$_3$ and PPh$_3$] were prepared from 1a and 1b by oxidative decarbonylation of the parent compound upon treatment of Me$_3$NO in the presence of a P-donor. Similar reactions between 1a and 1b and the diphosphines dppm and dppf were also confirmed. The $\eta^4$-coordination of a phenazine and acridine ligand to the iron center in our new compounds is unprecedented, and we have structurally established this phenomenon in for compounds 1a, 2a, 3b, and 4a. The stability of the ancillary phenazine and acridine ligands in arene exchange reactions and site-selective functionalization of the coordinated heterocycle are presently under investigation.

5. Acknowledgements

We thank the Ministry of Education, the Government of the People’s Republic of Bangladesh for financial support. MGR thanks the Robert A. Welch Foundation (grant B-1093) for financial support and acknowledges computational resources through UNT's High Performance Computing Services and CASCaM. Prof. Michael B. Hall (TAMU) is thanked for providing us a copy of his JIMP2 program, which was used to prepare the geometry-optimized structure reported here.

6. Appendix A. Supplementary material

CCDC .........., CCDC .........., CCDC .......... and CCDC.......... contain supplementary crystallographic data for 1a, 2a, 3b and 4a successively. These data may be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
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Fig. 1. ORTEP drawing of the molecular structure of Fe(CO)$_3$(η$^4$-C$_{12}$H$_8$N$_2$) (1a; top) and DFT-optimized structure of A (bottom). Selected X-ray diffraction bond lengths (Å) and angles (°): Fe(1)-C(5) 2.0549(19), Fe(1)-C(6) 2.057(2), Fe(1)-C(4) 2.154(2), Fe(1)-C(7) 2.156(2), N(1)-C(8) 1.308(2), N(1)-C(11) 1.386(2), N(2)-C(9) 1.312(2), N(2)-C(10) 1.394(2), C(4)-C(5) 1.430(3), C(4)-C(9) 1.468(2), C(5)-C(6) 1.395(3), C(6)-C(7) 1.425(3), C(7)-C(8) 1.471(3), C(8)-C(9) 1.432(3), C(10)-C(11) 1.403(3), C(12)-C(13) 1.377(3), C(13)-C(14) 1.393(3), C(14)-C(15) 1.376(3), C(2)-Fe(1)-C(1) 91.51(10), C(2)-Fe(1)-C(3) 100.58(9), C(1)-Fe(1)-C(3) 99.56(9), C(2)-Fe(1)-C(5) 93.34(9), C(1)-Fe(1)-C(5) 124(9), C(3)-Fe(1)-C(5) 133.57(9), C(2)-Fe(1)-C(6) 122.76(9), C(1)-Fe(1)-C(6) 94.26(9), C(3)-Fe(1)-C(6) 134.03(9), C(5)-Fe(1)-C(6) 39.68(8), C(2)-Fe(1)-C(4) 93.95(8), C(1)-Fe(1)-C(4) 163.29(9), C(3)-Fe(1)-C(4) 94.94(9), C(5)-Fe(1)-C(4) 39.64(8), C(6)-Fe(1)-C(4) 69.55(8), C(2)-Fe(1)-C(7) 161.87(9), C(1)-Fe(1)-C(7) 93.49(9), C(3)-Fe(1)-C(7) 95.76(8), C(5)-Fe(1)-C(7) 69.52(8), C(6)-Fe(1)-C(7) 39.47(8), C(4)-Fe(1)-C(7) 76.75(8).
Fig. 2. ORTEP drawing of the molecular structure of Fe(CO)$_2$(P(OMe)$_3$)(η$^4$-C$_{12}$H$_8$N$_2$) (2a). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)-P(1) 2.1647(6), Fe(1)-C(1) 1.773(4), Fe(1)-C(2) 1.772(4), Fe(1)-C(6) 2.153(4), Fe(1)-C(7) 2.048(4), Fe(1)-C(8) 2.050(4), Fe(1)-C(9) 2.153(4), C(14)-C(15) 1.376(5), C(15)-C(16) 1.396(5), N(1)-C(10) 1.308(5), N(1)-C(11) 1.371(4), N(2)-C(16) 1.394(4), N(2)-C(17) 1.305(5), C(6)-C(7) 1.428(5), C(6)-C(17) 1.472(5), C(7)-C(8) 1.408(4), C(8)-C(9) 1.423(5), C(9)-C(10) 1.453(5), C(10)-C(17) 1.454(3), C(11)-C(12) 1.411(5), C(11)-C(16) 1.420(3), C(12)-C(1) 1.369(5), C(13)-C(14) 1.405(4), C(1)-Fe(1)-P(1) 95.94(13), C(2)-Fe(1)-P(1) 96.18(13), C(2)-Fe(1)-C(1) 90.99(11), C(8)-Fe(1)-P(1) 138.75(11), C(9)-Fe(1)-P(1) 99.77(11).
Fig. 3. ORTEP drawing of the molecular structure of Fe(CO)\textsubscript{2}(PPh\textsubscript{3})(\eta^{4}-C\textsubscript{13}H\textsubscript{9}N) (3b). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)-P(1) 2.2277(6), Fe(1)-C(4) 2.1585(19), Fe(1)-C(5) 2.054(2), Fe(1)-C(6) 2.051(2), Fe(1)-C(7) 2.143(2), N(1)-C(3) 1.321(3), N(1)-C(15) 1.399(3), C(3)-C(4) 1.469(3), C(4)-C(5) 1.422(3), C(5)-C(6) 1.406(3), C(6)-C(7) 1.432(3), C(7)-C(8) 1.466(3), C(3)-C(8) 1.434(3), C(4)-Fe(1)-P(1) 97.90(6), C(5)-Fe(1)-P(1) 92.74(6), C(5)-Fe(1)-C(4) 39.35(8), C(5)-Fe(1)-C(7) 69.78(8), C(6)-Fe(1)-P(1) 119.05(7), C(6)-Fe(1)-C(4) 69.60(8), C(6)-Fe(1)-C(5) 40.07(9), C(6)-Fe(1)-C(7) 39.86(9), C(7)-Fe(1)-P(1) 158.90(6), C(7)-Fe(1)-C(4) 76.33(8), C(6)-C(7)-Fe(1) 66.59(11), C(6)-C(7)-C(8) 119.87(18), C(8)-C(7)-Fe(1) 104.24(13), C(3)-C(8)-C(7) 114.45(18), C(9)-C(8)-C(3) 120.0(2), C(9)-C(8)-C(7) 125.44(19), C(8)-C(9)-C(10) 118.6(2), N(1)-C(3)-C(4) 121.45(18), N(1)-C(3)-C(8) 123.56(19), C(8)-C(3)-C(4) 114.88(18), C(3)-C(4)-Fe(1) 103.35(12), C(5)-C(4)-Fe(1) 66.35(11), C(5)-C(4)-C(3) 119.80(19), C(4)-C(5)-Fe(1) 74.31(11), C(6)-C(5)-Fe(1) 69.85(12), C(6)-C(5)-C(4) 116.45(19), C(5)-C(6)-Fe(1) 70.08(12), C(5)-C(6)-C(7) 115.60(19), C(7)-C(6)-Fe(1) 73.56(12).
Fig. 4. ORTEP drawing of the molecular structure of Fe(CO)₂(dpdp)(η⁴-C₁₂H₈N₂) (4a). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)–C(1) 1.758(4), Fe(1)–C(2) 1.773(4), Fe(1)–C(4) 2.031(4), Fe(1)–C(5) 2.038(4), Fe(1)–C(3) 2.122(4), Fe(1)–C(6) 2.133(4), Fe(1)–P(1) 2.2081(12), C(3)–C(4) 1.409(5), C(3)–C(16) = 1.453(5), C(4)–C(5) 1.392(5), C(5)–C(6) 1.416(5), C(6)–C(7) 1.451(5), C(7)–C(8) 1.283(5), C(7)–C(16) 1.452(5), C(8)–C(9) 1.366(5), C(9)–C(10) 1.405(5), C(9)–C(14) 1.408(5), C(10)–C(11) = 1.359(5), C(11)–C(12) 1.398(6), C(12)–C(13) 1.375(6), C(1)–Fe(1)–C(2) 100.73(17), C(1)–Fe(1)–C(4) 123.03(17), C(2)–Fe(1)–C(4) 134.58(16), C(1)–Fe(1)–C(5) 92.71(16), C(2)–Fe(1)–C(5) 137.41(16), C(4)–Fe(1)–C(5) 40.01(15), C(1)–Fe(1)–C(3) 162.11(16), C(2)–Fe(1)–C(3) 95.54(16), C(4)–Fe(1)–C(3) 39.60(15), C(5)–Fe(1)–C(3) 70.09(15), C(1)–Fe(1)–C(6) 93.04(16), C(2)–Fe(1)–C(6) 98.96(16), C(4)–Fe(1)–C(6) 69.59(15), C(5)–Fe(1)–C(6) 39.62(15), C(3)–Fe(1)–C(6) 76.99(15), C(1)–Fe(1)–P(1) 89.19(13), C(2)–Fe(1)–P(1) 100.29(12), C(4)–Fe(1)–P(1) 92.47(12), C(5)–Fe(1)–P(1) 120.30(12), C(3)–Fe(1)–P(1) 95.22(11), C(6)–Fe(1)–P(1) 159.85(11).
References


34 (a) JIMP2, version 0.091, a free program for the visualization and manipulation of molecules: M. B. Hall, R. F. Fenske, Inorg. Chem. 11 (1972) 768. (b) J. Manson, C. E. Webster, M. B. Hall, Texas A&M University, College Station, TX, 2006: http://www.chem.tamu.edu/jimp2/index.html.


