Electronic Supplementary Material (ESI) for Chemical Communications

The metal–carbonyl…π(aryl) interaction as a supramolecular synthon for the stabilisation of transition metal carbonyl crystal structures

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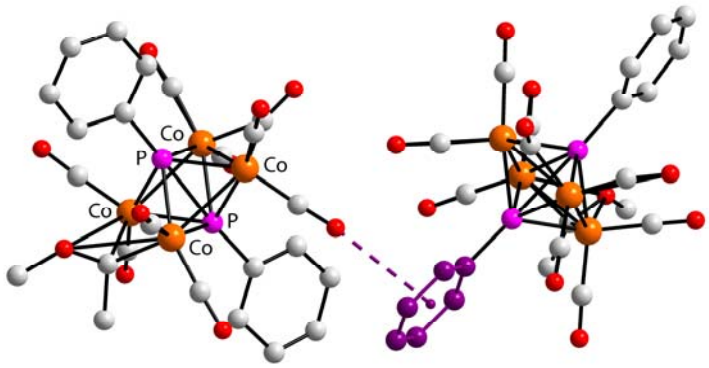
**** SUPPLEMENTARY MATERIAL ****

PART A: Supramolecular aggregation patterns sustained by metal-carbonyl(lone pair)…π interactions.
PART B: Plots of geometric parameters, α, β and *d*.

PART A: Supramolecular aggregation patterns sustained by metal-carbonyl(lone pair)…π interactions.

Zero-dimensional aggregation patterns based on M–carbonyl(lone pair)…π(aryl) interactions

MOTIF 1: Two-molecule aggregates sustained by a single M–carbonyl(lone pair)…π(aryl) interaction

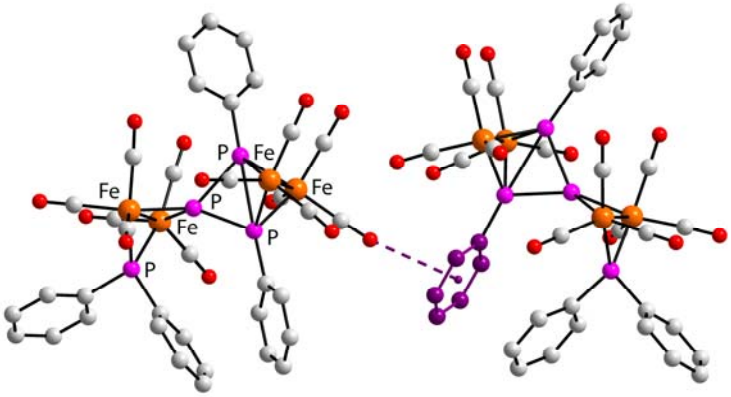


3.26 Å; 9.9°; 173.5°

FERTEB

Octacarbonyl-(μ$_2$-carbonyl)-(μ$_2$-1-methoxyethylidene)-bis(μ$_4$-phenylphosphinidene)-tetra-cobalt

[M.G. Richmond and J.K. Kochi, *Organometallics*, 1987, **6**, 777]

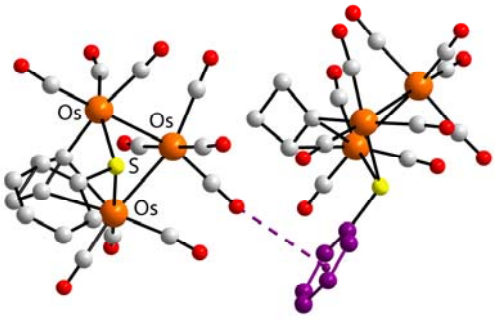


3.35 Å; 7.1°; 163.2°

GATGEN

(μ$_4$-1,3-Diphenyl-triphosphine-P,P,P',P',P'',P'')-(μ$_2$-diphenylphosphido-P,P)-dodecacarbonyl-tetra-iron

[S. Attali, F. Dahan, R. Mathieu, A.-M. Caminade and J.-P. Majoral, *J. Am. Chem. Soc*., 1988, **110**, 1990]

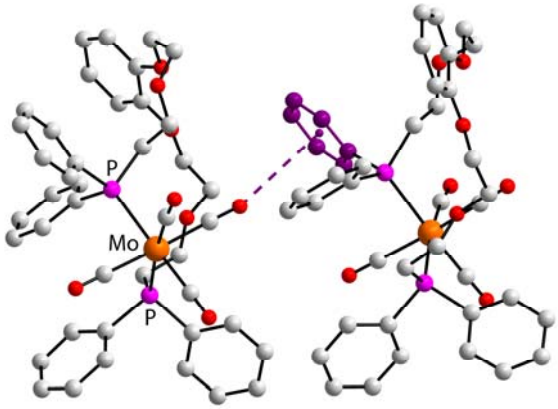


3.45 Å; 0.6°; 162.5°

LACMUX10

(μ_2-Phenylthiolato)(μ_2-η^2,σ^1-cyclobutenyl)-decacarbonyl-triangulo-tri-osmium

[R.D. Adams, G. Chen, X. Qu, W. Wu and J.H. Yamamoto, *Organometallics*, 1993, **12**, 3029]



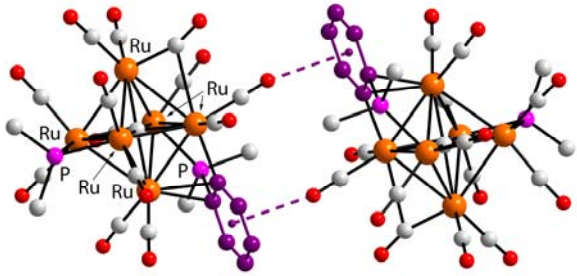
3.52 Å; 7.6°; 161.2°

NAPZUZ01

cis-(1,2-bis(7,7-Diphenyl-1,4-dioxa-7-phosphaheptyl)benzene-P,P')-tetracarbonyl-molybdenum

[C.H. Duffey, C.H. Lake and G.M. Gray, *Organometallics*, 1998, **17**, 3550]

MOTIF 2: Two molecule aggregates sustained by two M–carbonyl(lone pair)…π(aryl) interactions

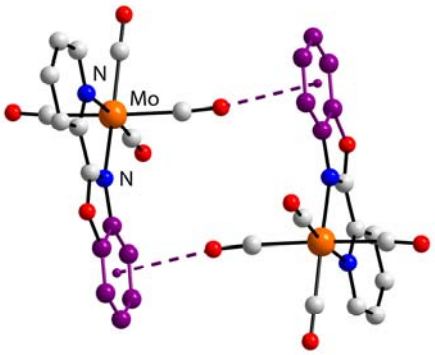


2.94 Å; 4.3°; 165.1°

MOVVOI

(μ_6-Carbido)-(μ_3-η^2-dimethylphenylphosphine)-(μ_2-dimethylphosphido)-tridecacarbonyl-hexa-ruthenium

[R.D. Adams, B. Captain, W. Fu and M.D. Smith, *J. Organomet. Chem.*, 2002, **651**, 124]

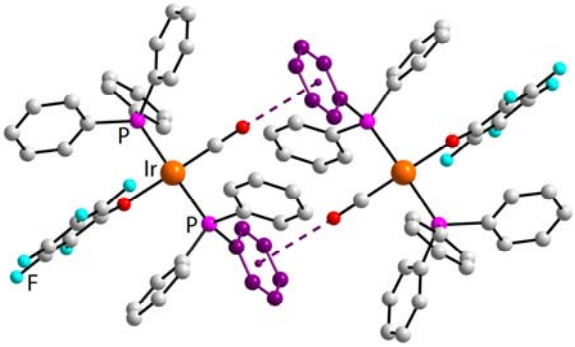


3.12 Å; 6.9°; 160.3°

EJOSAY

tetracarbonyl-(2-(pyridin-2-yl)-1,3-benzoxazole)-molybdenum

[P. Datta, D. Sardar, A.P. Mukhopadhyay, E. Lopez-Torres, C.J. Pastor and C. Sinha, *J. Organomet. Chem.,* 2011, **696**, 488]

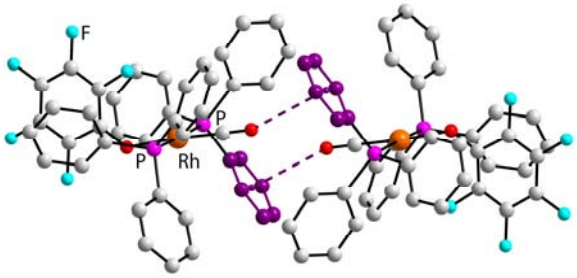


3.25 Å; 6.1°; 161.2°

DUZJUD

trans-Carbonyl-(pentafluorophenoxy-O)-bis(triphenylphosphine)-iridium(i)

[M.R. Churchill, J.C. Fettinger, W.M. Rees and J.D. Atwood, *J.Organomet.Chem.*, 1986, **308**, 361]

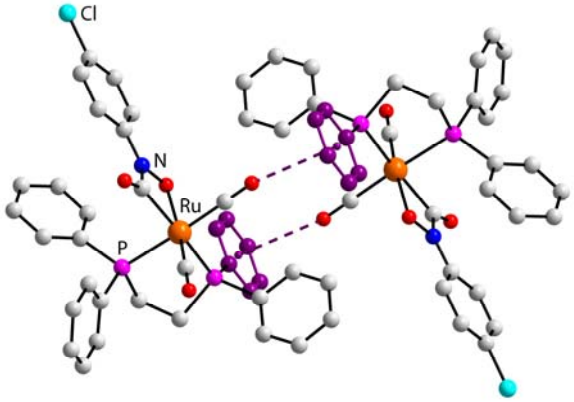


3.26 Å; 5.4°; 160.0°

DACCUG

Carbonyl-(perfluorophenolato)-bis(triphenylphosphino)-rhodium(I)

[K. Osakada and H. Ishii, *Inorg. Chim. Acta*, 2004, **357**, 3007]

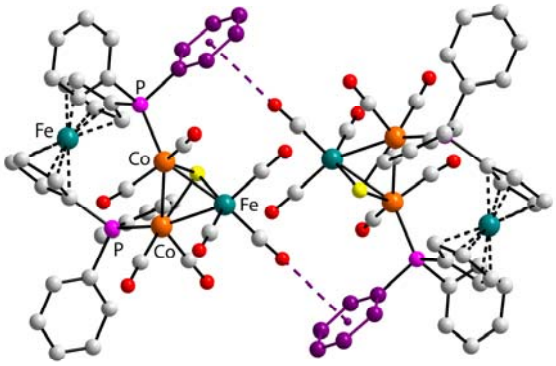


3.27 Å; 3.3°; 169.3°

VIRFEH10

(1,2-bis(Diphenylphosphino)ethane-P,P')-(N-oxy-N-(p-chlorophenyl)-carbamato-C,O)-dicarbonyl-ruthenium

[J.D. Gargulak, A.J. Berry, M.D. Noirot and W.L. Gladfelter, *J. Am. Chem. Soc*., 1992, **114**, 8933]

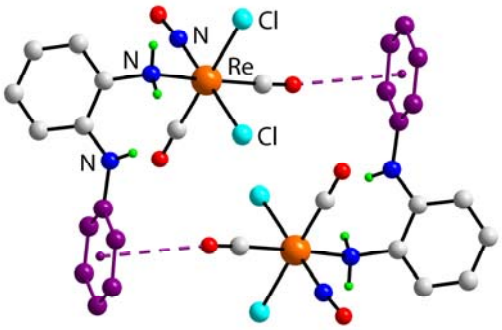


3.28 Å; 6.9°; 176.0°

AJOLIU01

(μ_3-Sulfido)-(m2-1,1'-bis(diphenylphosphino)ferrocene-P,P')-heptacarbonyl-di-cobalt-iron dichloromethane solvate

[H. Zhang, Q.-L. Suo, Y.-B. Wang, L. Wang, L.-H. Weng and X.-B. Leng, *Acta Phys. Sin*., 2002, **18**, 746]

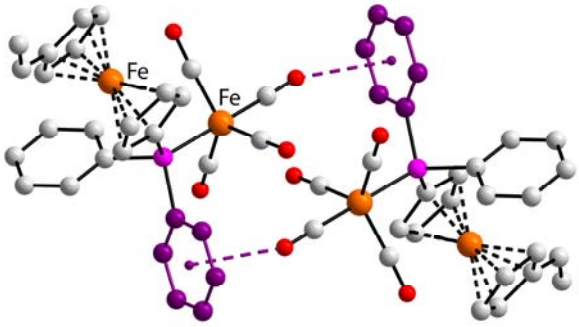


3.30 Å; 6.5°; 161.8°

UCALUF

Dichloro-dicarbonyl-(N-phenyl-o-phenylenediamine-N)-nitrosyl-rhenium benzene solvate

[A.A. Reshetnikov, M.O. Talismanova, A.A. Sidorov, S.E. Nefedov, I.L. Eremenko and I.I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.) (Russ. Chem. Bull.)*, 2001, 136]

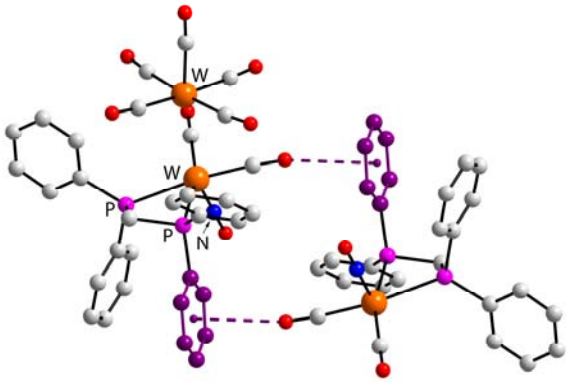


3.32 Å; 2.9°; 161.9°

NIVDAY

(1-(Diphenylphosphino)-1'-vinylferrocene)-tetracarbonyl-iron(0)

[P. Stepnicka, *J. Organomet. Chem*., 2008, **693**, 297]

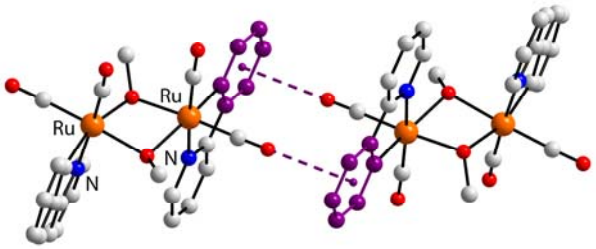


3.35 Å; 5.0°; 166.7°

KESPUT

(μ_2-Hydrido)-(bis(diphenylphosphino)methane-P,P')-nitrosylheptacarbonyl-di-tungsten

[J.T. Lin, S.Y. Wang, P.S. Huang, Y.M. Hsiao, Y.S. Wen and S.K. Yeh, *J. Organomet. Chem*., 1990, **388**, 151]

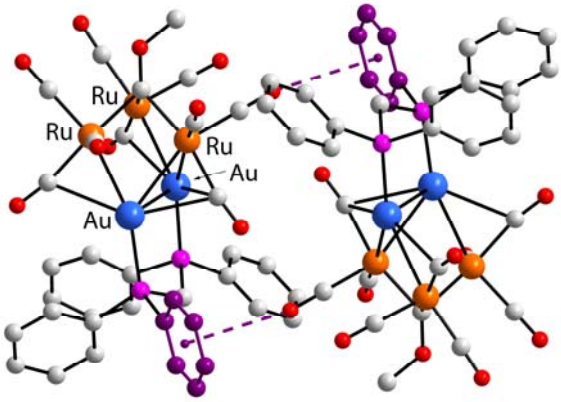


3.37 Å; 8.3°; 174.5°

DOHTAW

cis-bis(μ_2-Methoxo)-bis(2-(2-pyridyl)phenyl-C,N)-tetracarbonyl-diruthenium

[G. Maas, L. Schaeffler and S. Buck, *Z. Naturforsch., B: Chem. Sci*., 2008, **63**, 977]

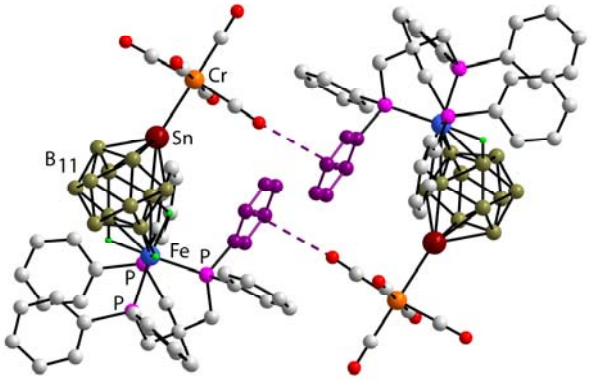


3.40 Å; 8.5°; 168.2°

SAFMAN

(μ_3-Methoxymethylidyne)-(μ_2-hydrido)-(μ_2-bis(diphenylphosphido)methane)-nonacarbonyl-di-gold-tri-ruthenium

[C.A. Collins, I.D. Salter, V. Sik, S.A. Williams and T. Adatia, *J. Chem. Soc., Dalton Trans.,* 1998, 1107]

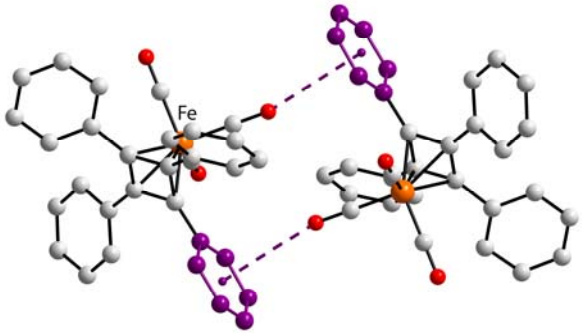


3.42 Å; 0.3°; 172.8°

MEMRUS

1-(Pentacarbonyl-chromium)-2,7,8-tri-μ-H-((1,1,1-tris (diphenylphosphinomethyl) ethane)-iron)-1-stanna-closododecaborate tetrahydrofuran solvate

[T. Gadt, K. Eichele and L. Wesemann, *Organometallics*, 2006, **25**, 3904]

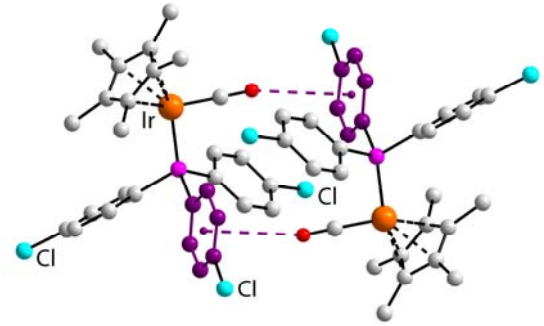


3.50 Å; 7.4°; 167.7°

PCYFCO

Tetraphenylcyclobutadiene iron tricarbonyl

[R.P. Dodge and V.Schomaker, *Acta Crystallogr*., 1965, **18**, 614]

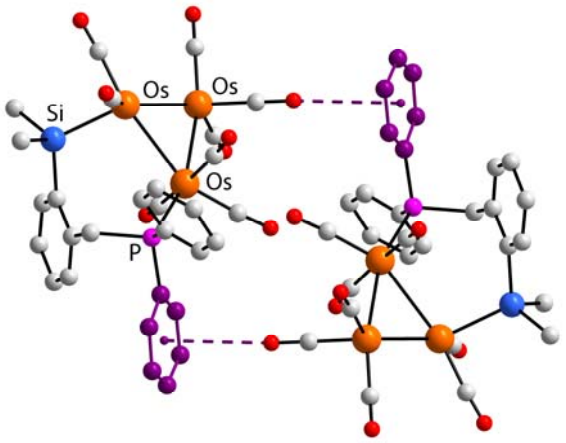


3.51 Å; 9.5°; 164.9°

RUHGAC

Carbonyl-(tris(p-chlorophenyl)phosphine) phosphine)-(η^5-pentamethylcyclopentadienyl)-iridium(i)

[D. Wang, R.J. Angelici, L.M. Thomas and R.A. Jacobson, *Z. Kristallogr*., 1997, **212**, 245]

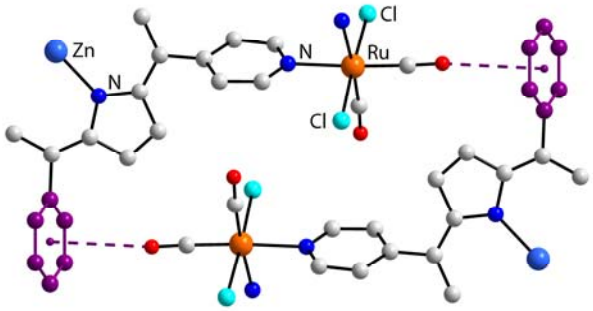


3.52 Å; 1.6°; 174.1°

YAFWAD

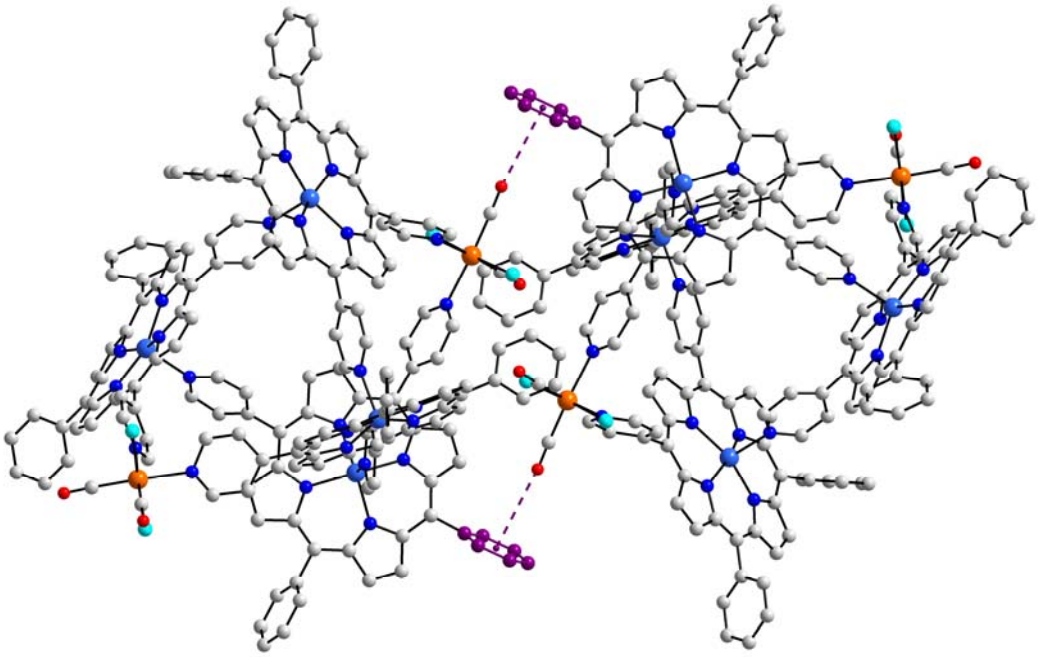
(μ_2-(2-(Diphenylphosphinomethyl)phenyl)dimethylsilyl-P,Si)-octacarbonyl-tris(μ_2-hydrido)-tri-osmium

[H. G. Ang, B. Chang and W. L. Kwik, *J. Chem. Soc., Dalton Trans*., 1992, 2161]



For reasons of clarity, hydrogen atoms have been removed from both images.

The upper view provides a detail of the nature of the Ru–carbonyl(lone pair)…π(aryl) interactions as the fragment is somewhat obscured in the complete molecule (lower view).

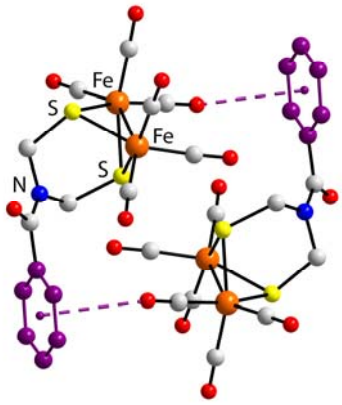


3.55 Å; 5.9°; 168.1°

WUFJUC

meso-trans,cis,cis-tetrakis((μ$_3$-cis-5,10-bis(4'-Pyridyl)-15,20-diphenylporphyrinato)-zinc(II))-bis(dichloro-dicarbonyl-ruthenium(II)) n-hexane chloroform solvate

[E. Iengo, E. Zangrando, S. Geremia, R. Graff, B. Kieffer and E. Alessio, *Chem.-Eur. J.*, 2002, **8**, 4670]

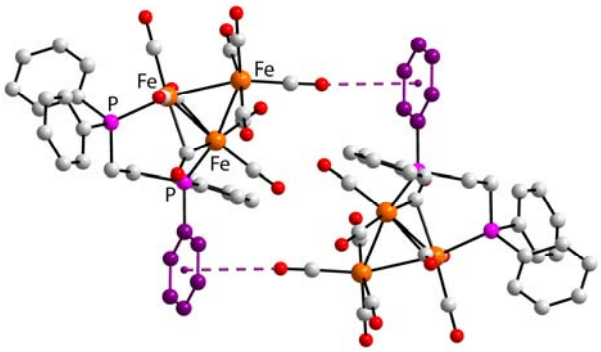


3.57 Å; 3.9°; 162.1°

QICKOD

(μ$_2$-N,N-bis((sulfanyl)methyl)phenyl-4-carboxamidato)-hexacarbonyl-diiron methanol solvate

[L.-C. Song, M.-Y. Tang, S.-Z. Mei, J.-H. Huang and Q.-M. Hu, *Organometallics*, 2007, **26**, 1575]

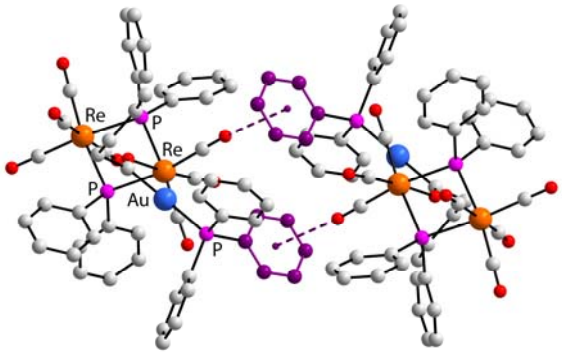


3.60 Å; 8.5°; 174.5°

XAPKAA

bis(μ_2-Carbonyl)-(μ_2-1,2-bis(diphenylphosphino)ethane)-octacarbonyltri-iron dichloromethane solvate

[H. Adams, S.C.M. Agustinho, B.E. Mann and S. Smith, *J. Organomet. Chem*., 2000, **607**, 175]

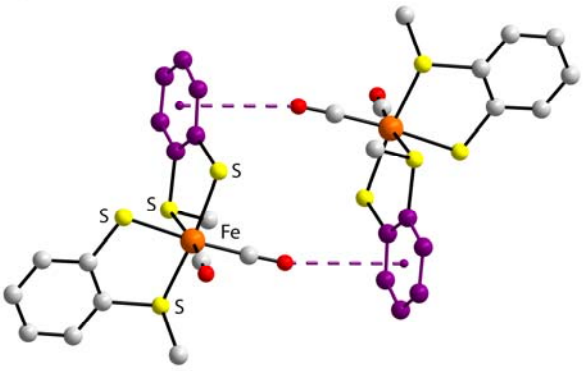


3.65 Å; 9.5°; 162.7°

POYYUX

bis(μ_2-Diphenylphosphido)-(μ_2-valeryl-C,O)-heptacarbonyl-(triphenylphosphine)-gold(I)-di-rhenium chloroform solvate

[H.-J. Haupt, D. Petters and U. Florke, *J. Organomet. Chem.*, 1998, **553**, 497]

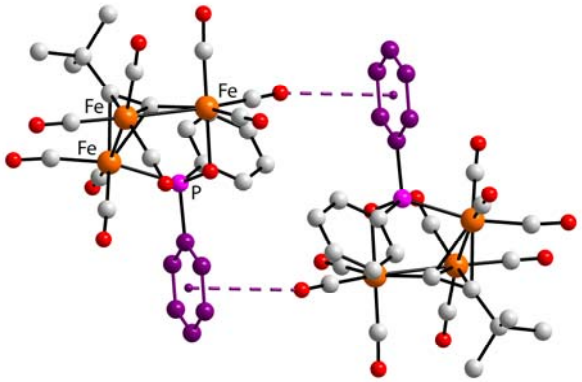


3.70 Å; 8.2°; 168.3°

CECBOB

Dicarbonyl-bis(o-methylthiobenzenethiolato-S,S')-iron(II)

[D. Sellmann, G. Lanzrath, G. Huttner, L. Zsolnai, C. Kruger and K.H. Claus, *Z. Naturforsch., B:Chem.Sci*., 1983, **38**, 961]

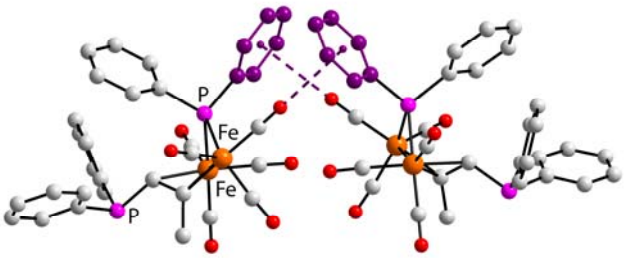


3.75 Å; 6.2°; 161.2°

FUJLOL

(μ_3-η^4-σ^1 -t-Butylacetylenyl)-nonacarbonyl-(μ_2-diphenylphosphidoxo-O, P)-tri-iron

[D.E. Fogg, N.J. Taylor, A. Meyer and A.J. Carty, *Organometallics*, 1987, **6**, 2252]



3.36 Å; 5.5°; 179.3°

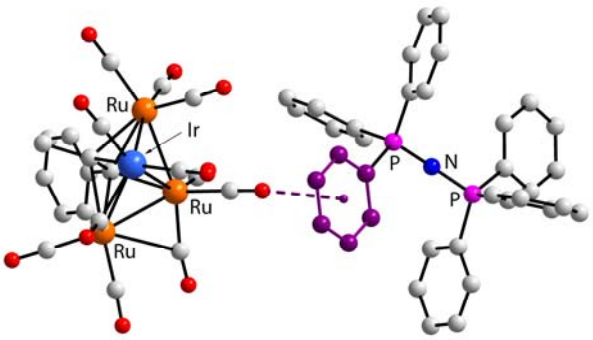
TEBLAN

(μ_2-η^2-1-(Diphenylphosphino)propen-2-yl)-(μ_2-diphenylphosphido)-hexacarbonyl-di-iron

[S. Doherty, M.R.J. Elsegood, W. Clegg, T.H. Scanlan and N.H. Rees, *Chem.Commun.*, 1996, 1545]

*The preceding molecules having Motif **2** are centrosymmetric. In this structure, the dimeric aggregate has 2-fold symmetry.*

MOTIF 3: Two molecule aggregates sustained by one M–carbonyl(lone pair)…π(aryl) interaction {dissimilar molecules}

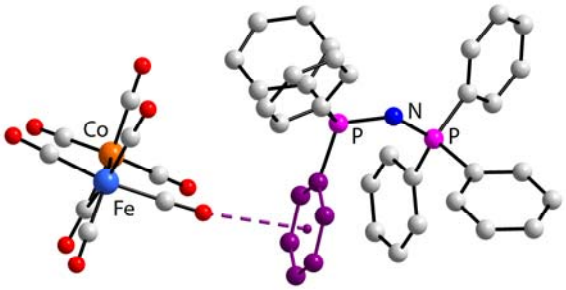


3.13 Å; 9.8°; 171.4°

FEXMEA

bis(Triphenylphosphoranylidene)ammonium (μ_4-η^4,σ^2-1-methyl-2-phenylacetylene)-(μ_2-carbonyl)-decacarbonyl-iridium-tri-ruthenium

[V. Ferrand, G. Suss-Fink, A. Neels and H. Stoeckli-Evans, *Eur. J. Inorg. Chem*., 1999, 853]

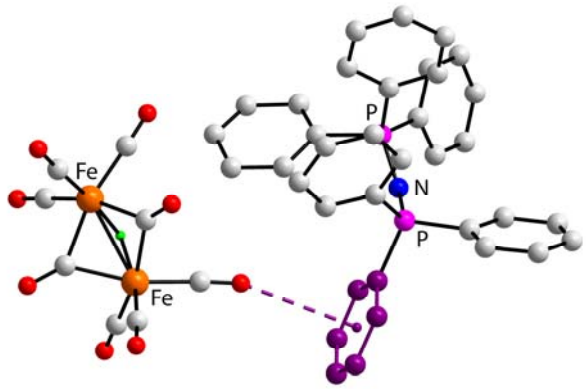


3.21 Å; 2.4°; 165.8°

TPICOF01

bis(Triphenylphosphine)iminium (μ_2-carbonyl)-heptacarbonyl-cobalt-iron

[P. Macchi, L. Garlaschelli and A. Sironi, *J. Am. Chem. Soc*., 2002, **124**, 14173]

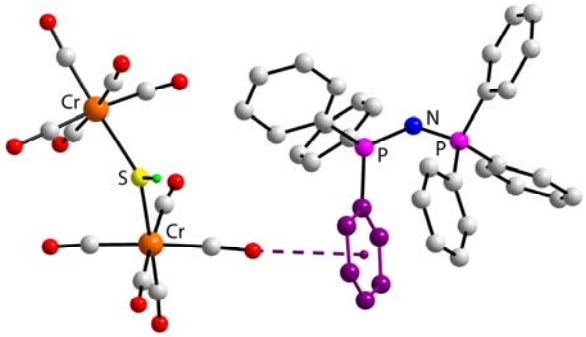


3.42 Å; 2.4°; 161.9°

TPIMFE

bis(Triphenylphosphine)iminium μ-hydrido-di- μ-carbonyl-bis(tricarbonyl-iron)

[H.B. Chin and R. Bau, *Inorg. Chem.,* 1978, **17**, 2314]

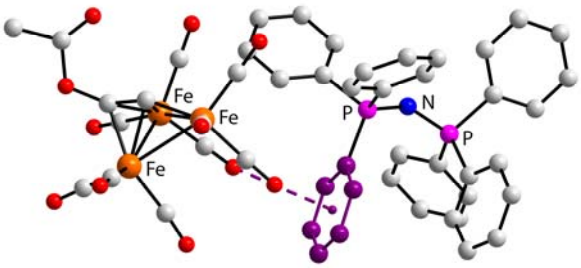


3.47 Å; 8.2°; 169.4°

JIHXUT

bis(Triphenylphosphine)iminium (μ_2-mercapto)-bis(pentacarbonyl-chromium)

[R.C. Hynes, K.F. Preston, J.J. Springs and A.J. Williams, *Organometallics*, 1991, **10**, 180]

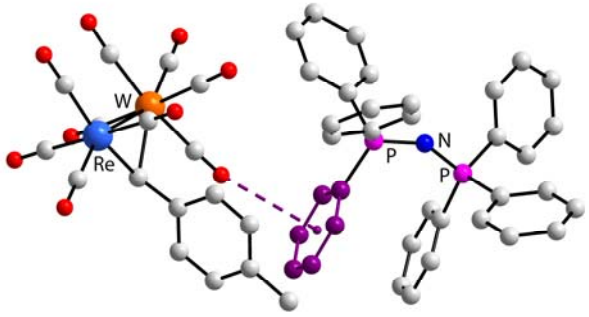


3.50 Å; 5.0°; 168.3°

DIKJAI10

bis(Triphenylphosphine)iminium nonacarbonyl-(μ_3-η^4,σ^1-acetyloxyacetylene)-tri-iron

[J.A. Hriljac and D.F. Shriver, *J. Am. Chem. Soc*., 1987, **109**, 6010]

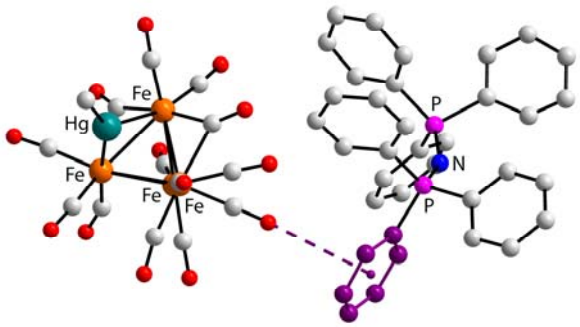


3.55 Å; 7.0°; 168.3°

CERRIA10

bis(Triphenylphosphine)-iminium 1,1,1,1,2,2,2,2,2-nonacarbonyl-(μ_2-p-tolylmethylene) -rhenium-tungsten

[J.C. Jeffery, A.G. Orpen, F.G.A. Stone and M.J. Went, *J. Chem. Soc*., *Dalton Trans*., 1986, 173]

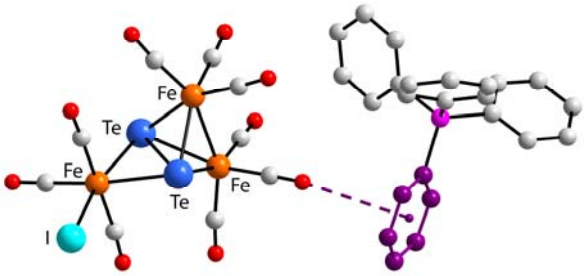


3.66 Å; 7.2°; 163.1°

DIKXOK

bis(Triphenylphosphine)-iminium tris(μ_2-carbonyl)-(μ_3-methyl-mercury) decacarbonyl-tetra-iron

[C.P. Horwitz, E.M. Holt, C.P. Brock and D.F. Shriver, *J. Am. Chem. Soc*., 1985, **107**, 8136]

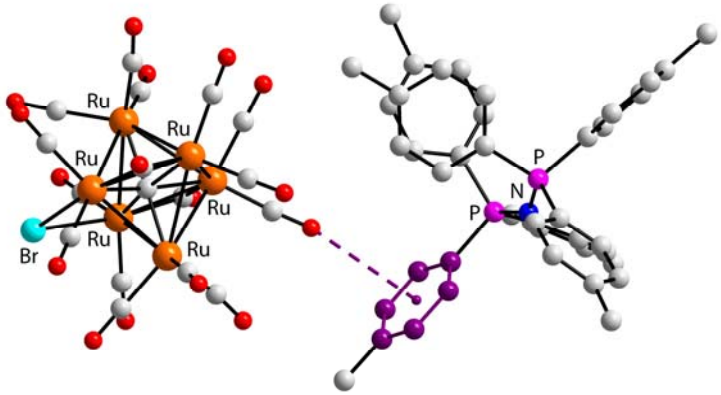


3.58 Å; 2.6°; 167.9°

YIKTUH

Tetraphenylphosphonium bis(μ_3-tellurido)-iodo-tris(tricarbonyl-iron)

[L.C. Roof, D.M. Smith, G.W. Drake, W.T. Pennington and J.W. Kolis, *Inorg. Chem*., 1995, **34**, 337]

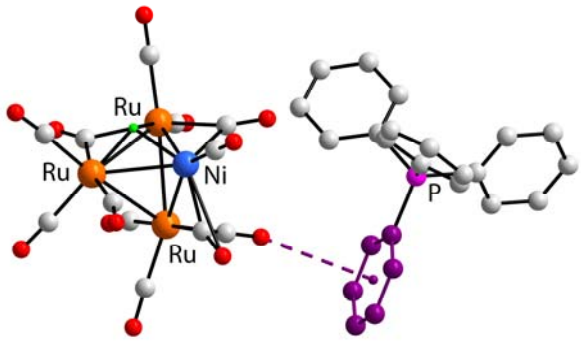


3.66 Å; 8.8°; 164.5°

YULKAR

bis(tris(p-Tolylyl)phosphine)iminium (μ_6-carbido)-bis(μ_2-carbonyl)-(μ_2 -bromo)-tetradecacarbonyl-hexa-ruthenium

[T. Chihara and H. Yamazaki, *J. Chem. Soc*., *Dalton Trans*., 1995, 1369]

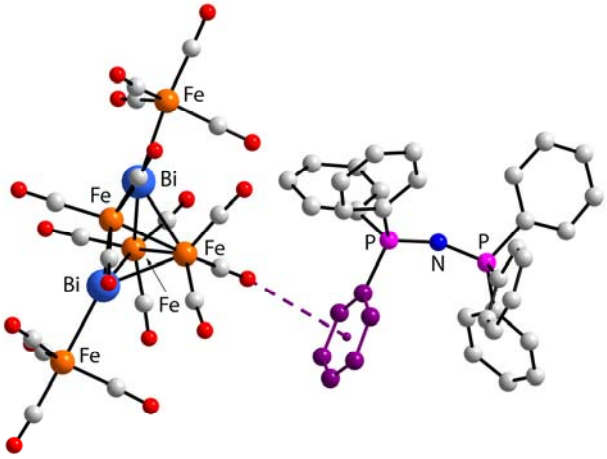


3.73 Å; 7.6°; 167.3°

ZECGAP

Tetraphenylphosphonium (μ_3-hydrido)-tetrakis(μ_2-carbonyl)-octacarbonyl-nickel-tri-ruthenium

[E. Brivio, A. Ceriotti, R.D. Pergola, L. Garlaschelli, M. Manassero and M. Sansoni, *J. Cluster Sci*., 1995, **6**, 271]

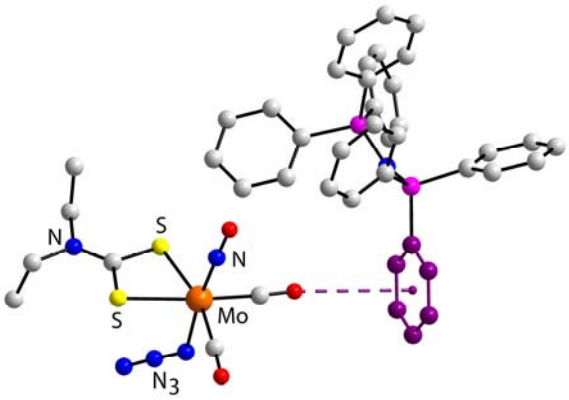


3.77 Å; 6.6°; 161.6°

WOXKAV

bis(bis(Triphenylphosphine)iminium) heptadecacarbonyl-di-bismuth penta-iron

[M. Rossignoli, R.C. Burns and D.C. Craig, *Aust. J. Chem*., 2000, **53**, 975]



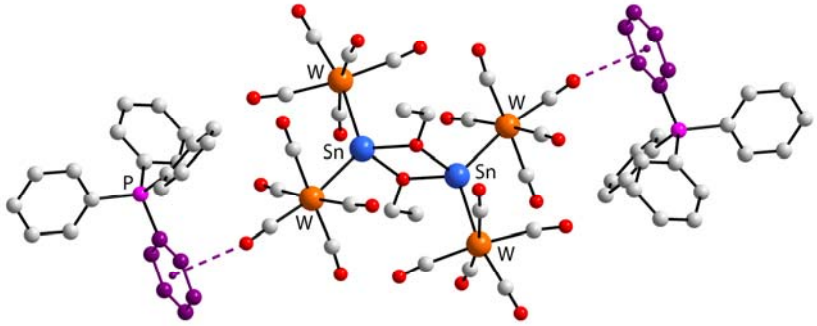
3.80 Å; 5.6°; 173.6°

YUDPUI

bis(Triphenylphosphine)iminium azido-dicarbonyl-(N,N-diethyldithiocarbamato-S,S')-nitroso-molybdenum(0)

[K.-B. Shiu, S.-T. Lin, S.-M. Peng and M.-C. Cheng, *Inorg. Chim. Acta*, 1995, **229**, 153]

MOTIF 4: Three molecule aggregates sustained by two M–carbonyl(lone pair)…π(aryl) interactions {dissimilar molecules}

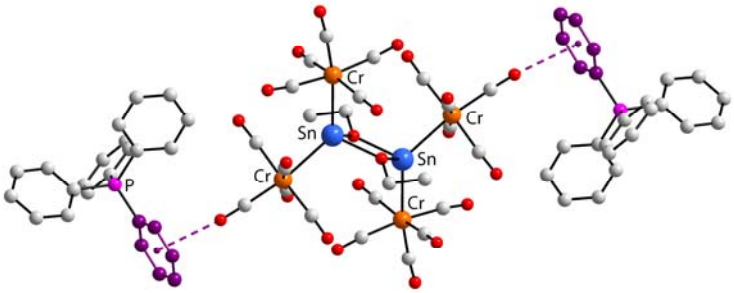


2.97 Å; 2.0°; 166.1°

PUHHIJ

bis((Tetraphenylphosphonium) (μ_2-ethoxo)-bis(pentacarbonyl-tungsten)-tin)

[P. Kircher, G. Huttner, K. Heinze and L. Zsolnai, *Eur. J. Inorg. Chem*., 1998, 1057]

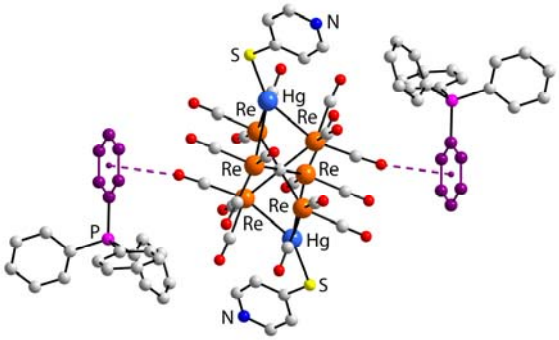


3.05 Å; 3.4°; 163.9°

PUHHUV

bis((Tetraphenylphosphonium) (μ_2-ethoxo)-bis(pentacarbonyl-chromium)-tin)

[P. Kircher, G. Huttner, K. Heinze and L. Zsolnai, *Eur. J. Inorg. Chem*., 1998, 1057]

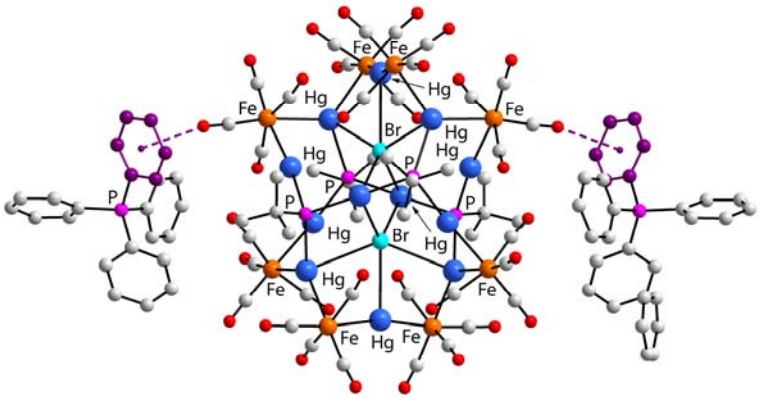


3.20 Å; 8.8°; 164.9°

DOLCIQ

bis(Tetraphenylphosphonium) (μ_6-carbido)-bis(4-pyridylthiolato)-octadecacarbonyl-di-mercury-hexa-rhenium

[U. Brand and J.R. Shapley, *Inorg. Chem*., 2000, **39**, 32]

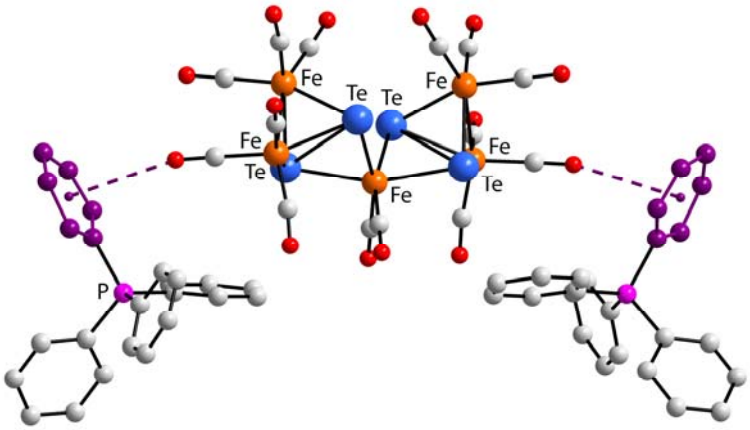


3.35 Å; 4.7°; 165.2°

HOXBAX

bis(Tetraphenylphosphonium) bis(μ_5-bromo)-tetrakis(μ_3-t-butylphosphinidene)-octakis(tetracarbonyl-iron)-dodeca-mercury toluene benzene solvate

[F. Hezel, D. Fenske, J. Eisenmann and T. Wetzel, *Z. Anorg. Allg. Chem*., 2000, **626**, 290]

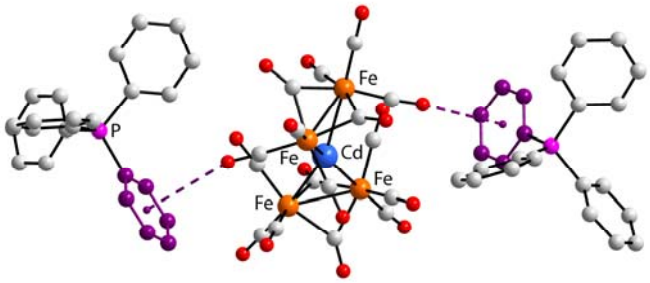


3.36 Å; 9.9°; 163.0°

VUHKIS

bis(Tetraphenylphosphonium) octadecacarbonyl-tetrakis(μ_3-telluride)-iron(II)-tetra-iron(I)

[L.C. Roof, W.T. Pennington and J.W. Kolis, *Angew. Chem., Int. Ed*., 1992, **31**, 913]

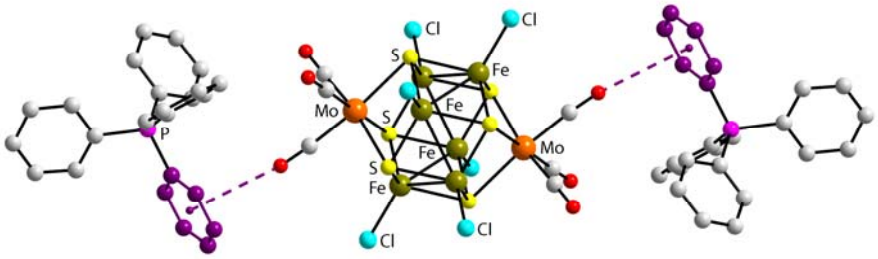


3.46 Å; 1.8°; 162.4°

TURXAF

bis(Tetraphenylphosphonium) tetrakis(μ$_2$-carbonyl)-dodecacarbonyl-cadmium-tetra-iron acetonitrile solvate

[V.G. Albano, M. Monari, F. Demartin, P. Macchi, C. Femoni, M.C. Iapalucci and G. Longoni, *Solid State Sciences*, 1999, **1**, 597]

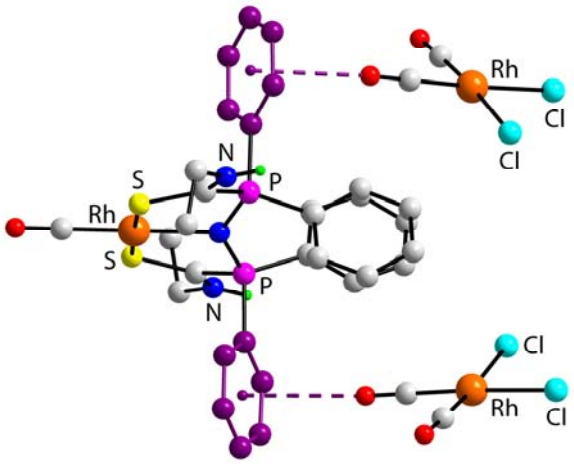


3.49 Å; 9.6°; 163.5°

DIKBII10

tetrakis(Tetraphenylphosphonium) hexacarbonyl-hexachloro-hexakis(μ$_4$-sulfido)-hexa-iron(II,III)-di-molybdenum(0) acetonitrile solvate

[D. Coucouvanis, A. Salifoglou, M.G. Kanatzidis, W.R. Dunham, A. Simopoulos and A. Kostikas, *Inorg. Chem*., 1988, **27**, 4066]



3.22 Å; 5.8°; 172.5°

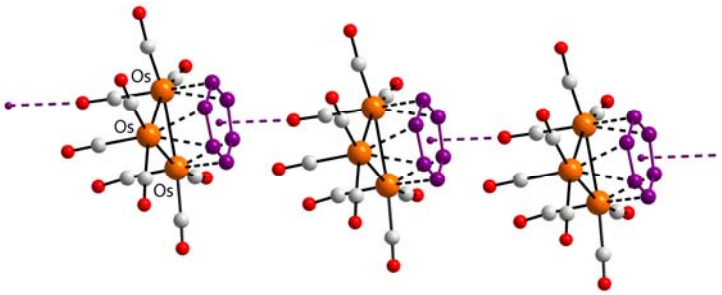
HIZWIX

(*N,N-bis((N-Ethylcarbamothioyl)(diphenyl)phosphoranylidene)ammonium-N,S,S')-carbonyl-rhodium(I) bis(dicarbonyl-dichloro-rhodium(I))*

[M. Delferro, D. Cauzzi, R. Pattacini, M. Tegoni, C. Graiffand and A. Tiripicchio, *Eur. J. Inorg. Chem*., 2008, 2302]

One- and three-dimensional aggregation patterns based on M–carbonyl(lone pair)…π(aryl) interactions

MOTIF 5: Linear supramolecular chains sustained by a single M–carbonyl(lone pair)…π(aryl) interaction

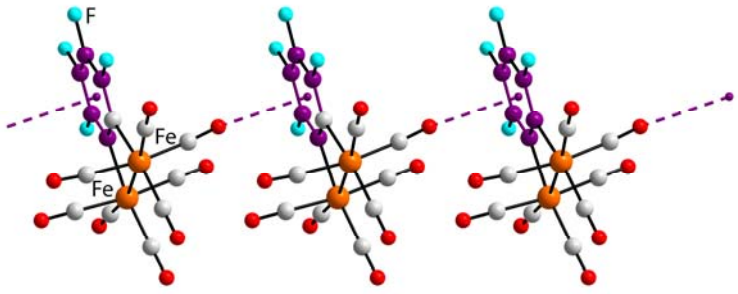


2.89 Å; 7.7°; 173.9°

DEMGEH10

(μ_3-η^2, η^2, η^2-Benzene)-nonacarbonyl-tri-osmium

[M.A. Gallop, M.P. Gomez-Sal, C.E. Housecroft, B.F.G. Johnson, J. Lewis, S.M. Owen, P.R. Raithby and A.H. Wright, *J. Am. Chem. Soc*., 1992, **114**, 2502]

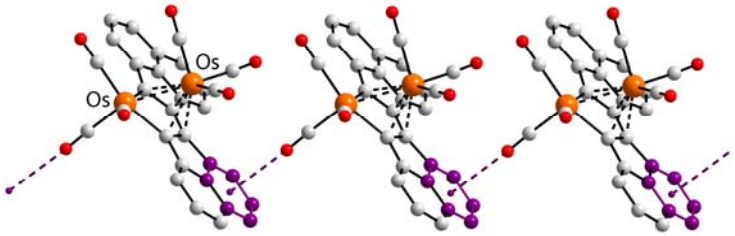


3.09 Å; 1.5°; 171.7°

TFPIOC

(μ_2-o-Tetrafluorophenylene)-octacarbonyl-di-iron

[M.J. Bennett, W.A.G. Graham, R.P. Srewart Jr and R.M. Tuggle, *Inorg. Chem.* 1973, **12**, 2944]

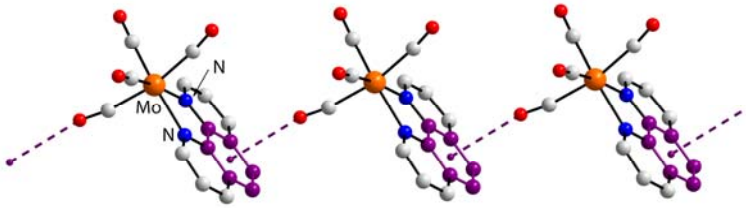


3.15 Å; 7.6°; 166.6°

ULUNEU

(μ_2-η^2, η^2-1,1'-Bi(acenaphthylen-2-yl))-hexacarbonyl-di-osmium

[R.D. Adams, B. Captain and J.L. Smith Jr., *J. Organomet. Chem*., 2003, **683**, 421]

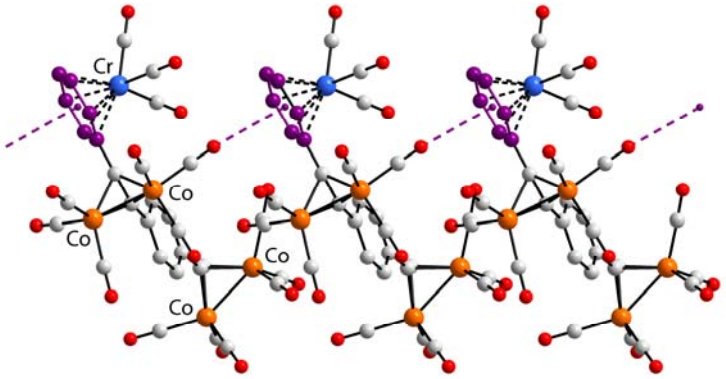


3.16 Å; 7.8°; 167.1°

DEDJUR01

Tetracarbonyl-(phenanthroline-N,N')-molybdenum(0)

[H.J. Bruins Slot, N.W. Murrall, and A.J. Welch, *Acta Crystallogr., Sect.C: Cryst. Struct. Commun*., **41**, 1309]

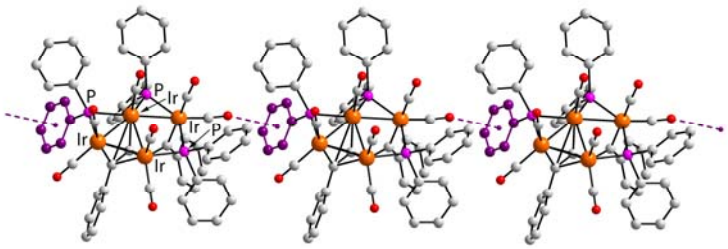


3.17 Å; 7.8°; 173.3°

QUBDOG

(μ_5-η^2, η^2, η^2, η^2-4-(η^6-phenylethynyl)phenylethyne)-dodecacarbonyltetra-cobalt-chromium

[F.-E. Hong, J.-W. Liaw, B.-J. Chien, Y.-C. Chang, C.-C. Lin, S.-L. Wang and F.-Ling Liao, *Polyhedron*, 1999, **18**, 2737]

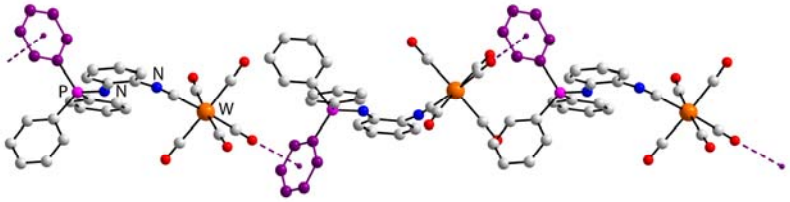


3.18 Å; 3.9°; 162.0°

TEHZOW

(μ_4-η^2-1,4-Diphenylbuta-1,3-diene-1,2,4-triyl)-tris(μ_2-diphenylphosphido)-heptacarbonyl-tetra-iridium benzene solvate

[M.H. Araujo, R.M.S. Pereira, M.D. Vargas, D. Braga and F. Grepioni, *J. Organomet. Chem*., 2005, **690**, 4611]

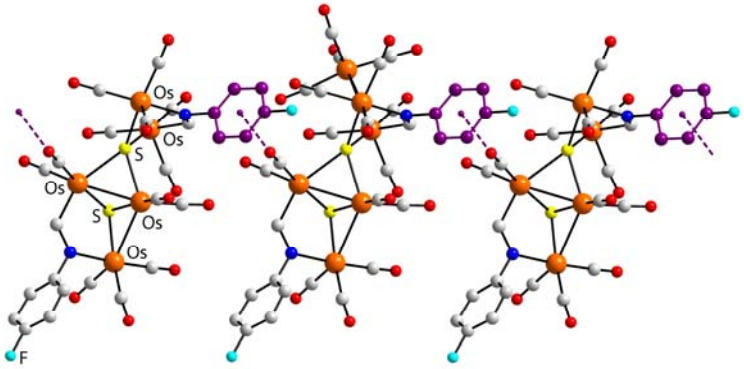


3.19 Å; 4.5°; 177.1°

XUZZOH

Pentacarbonyl-(2-(triphenylphosphinimino)phenyl isocyanide)-tungsten(0)

[F.E. Hahn, V. Langenhahn, N. Meier, T. Lugger and W.P. Fehlhammer, *Chem.-Eur. J*., 2003, **9**, 704]

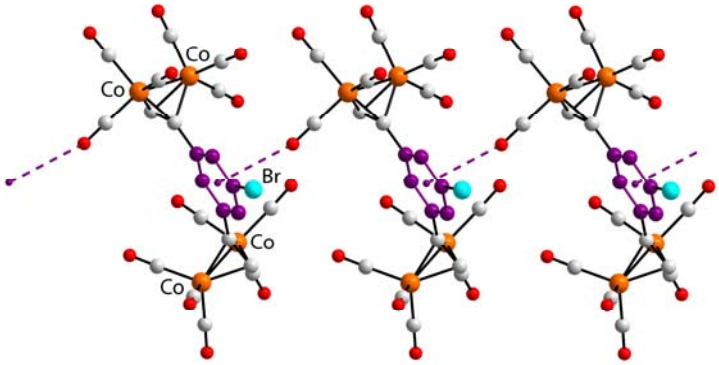


3.24 Å; 8.8°; 170.3°

BINGAG10

(μ_4-Sulfido)-(μ_3-sulfido)-bis(μ_2-hydrido)-bis(μ_2-N-(p-fluorophenyl)- formimidoyl)-heptadecacarbonyl-hexa-osmium

[R.D. Adams, Z. Dawoodi, D.F. Foust and B.E. Segmuller, *J. Am. Chem. Soc.*, 1983, **105**, 831]

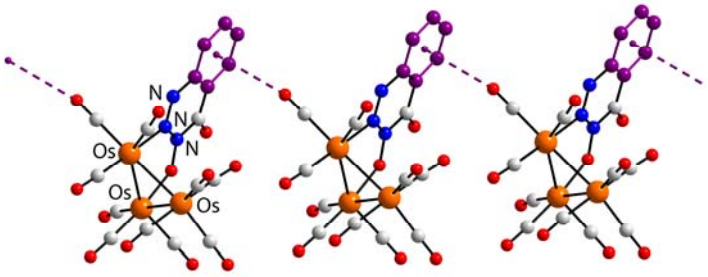


3.26 Å; 5.9°; 164.5°

NEQQIJ

(μ_4-η^2, η^2, η^2, η^2-5-bromo-1,3-bis(ethynyl)benzene)-bis(hexacarbonyl-dicobalt)

[S.M. Draper, M. Delamesiere, E. Champeil, B. Twamley, J.J. Byrne and C. Long, *J. Organomet. Chem.*, 1999, **589**, 157]

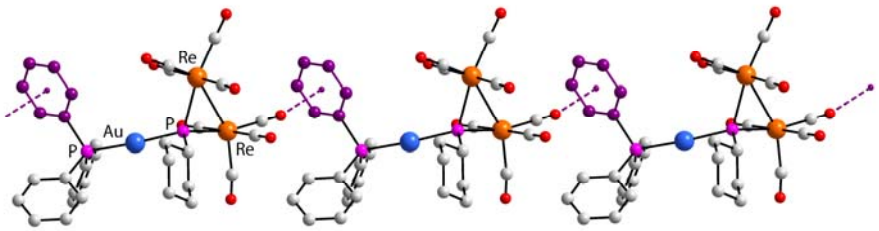


3.30 Å; 6.1°; 163.6°

GAQLUF

(μ_2-Hydrido)-(μ_2-3-hydroxy-1,2,3-benzotriazin-4(3H)-one)-decacarbonyl-tri-osmium

[S. Kumaresan, K.-L. Lu, J.-T. Hung, F.-Y. Lee, Y.-S.g Wen and J. R. Hwu, *J. Organomet. Chem.*, 1997, **549**, 155]

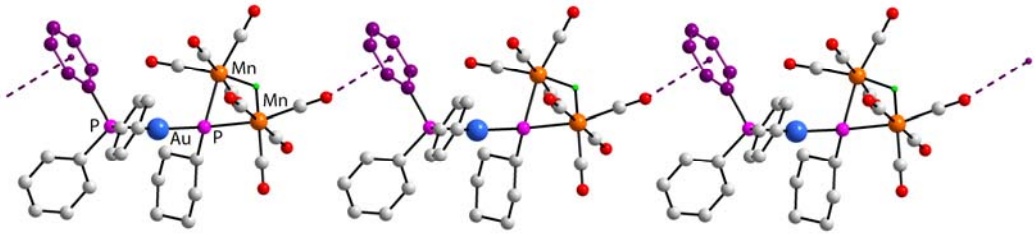


3.33 Å; 7.8°; 163.5°

YURJOK

(μ_3-Cyclohexylphosphido)-(μ_2-hydrido)-octacarbonyl-(triphenylphosphine-gold)-di-rhenium

[H.-J. Haupt, M. Schwefer and U. Florke, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1098]

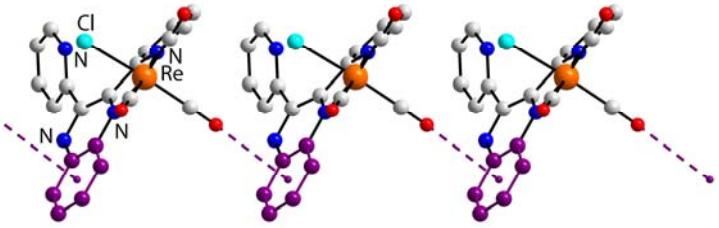


3.35 Å; 5.8°; 164.3°

ZIDSOU

(μ_3-Cyclohexylphosphino)-(μ_2-hydrido)-(triphenylphosphine-P)-octacarbonyl-gold-di-manganese

[H.-J. Haupt, M. Schwefer, H. Egold and U. Florke, *Inorg. Chem.*, 1995, **34**, 5461]

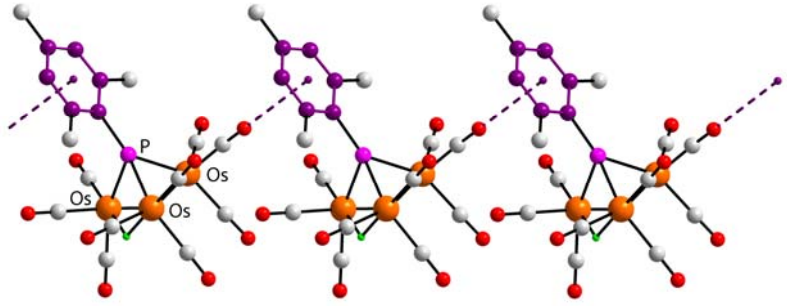


3.36 Å; 8.4°; 163.8°

PAYCUN

Tricarbonyl-chloro-(2,3-bis(2-pyridyl)quinoxaline)-rhenium(I)

[M.R. Waterland, T.J. Simpson, K.C. Gordon and A.K. Burrell, *J. Chem. Soc., Dalton Trans.*, 1998, 185]

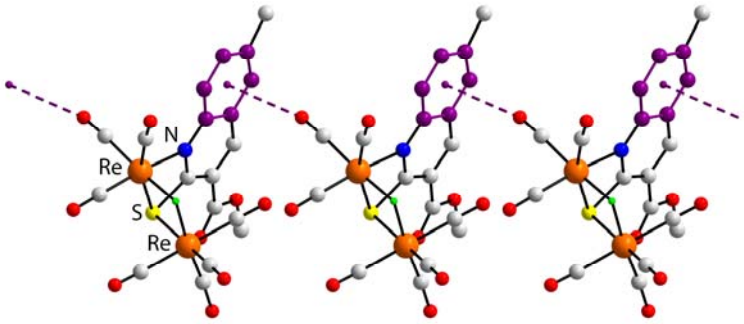


3.43 Å; 3.6°; 179.2°

WEGBOA

(μ_3-Mesitylphosphinidene)-bis(μ_2-hydrido)-nonacarbonyl-tri-osmium

[T. Kakizawa, H. Hashimoto and H. Tobita, *J. Organomet. Chem*., 2006, **691**, 726]

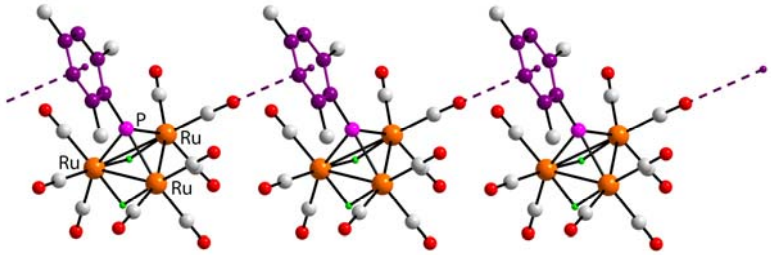


3.45 Å; 3.2°; 163.2°

LEDHAD

(μ_2-Hydrido)-(μ_2-6-methyl-3-methoxycarbonylquinoline-2-thiolato)-heptacarbonyl-di-rhenium

[R.D. Adams, Linfeng Chen and Wengan Wu, *Organometallic* , 1993, **12**, 4962]

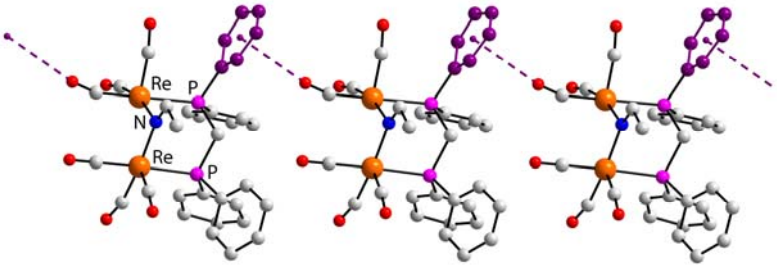


3.46 Å; 3.5°; 179.5°

WEFZIR

(μ_3-Mesitylphosphinidene)-bis(μ_2-hydrido)-nonacarbonyl-tri-ruthenium

[T. Kakizawa, H. Hashimoto and H.Tobita, *J. Organomet. Chem*., 2006, **691**, 726]

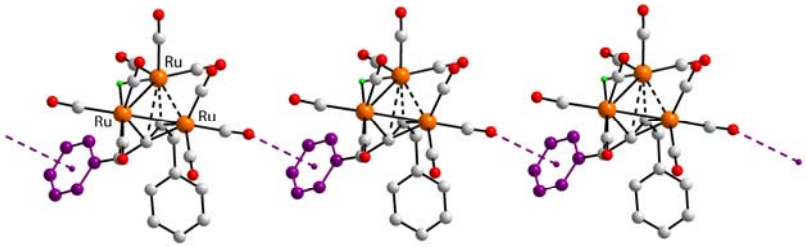


3.47 Å; 6.4°; 169.7°

PMEIRE10

(μ_2-bis(Diphenylphosphino)-methane)-(μ_2-ethylideneimino)-(μ_2-hydrido)-bis(tricarbonyl-rhenium)

[D.W. Prest, M.J. Mays and P.R. Raithby, *J. Chem. Soc., Dalton Trans*., 1982, 2021]

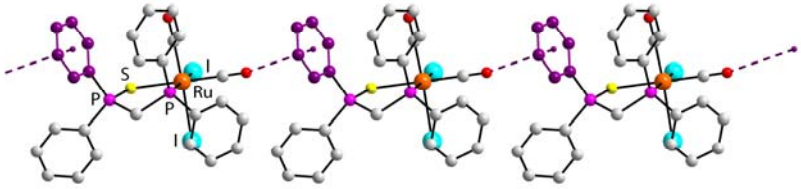


3.52 Å; 9.9°; 163.3°

VICNUQ

(μ_4-η^2, η^2-1,4-Diphenylbuta-1,2-diene-3-yl)-(μ_2-hydrido)-nonacarbonyltri-ruthenium

[L.P. Clarke, J.E. Davies, P.R. Raithby and G.P. Shields, *J. Chem. Soc., Dalton Trans*., 2000, 4527]

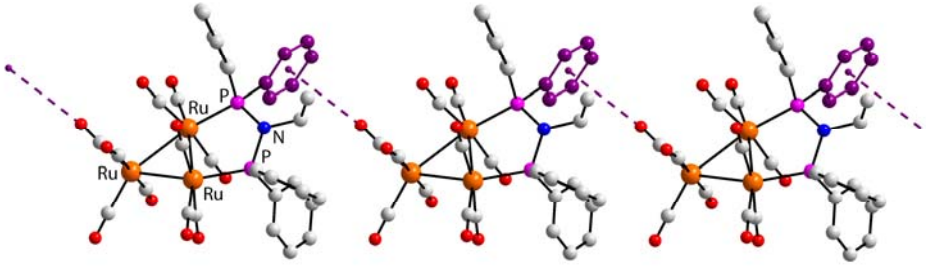


3.67 Å; 3.6°; 161.7°

YEDLOJ

Dicarbonyl-diiodo-((diphenylphosphinomethyl)diphenylphosphine sulfide-ruthenium(II)

[D.K. Dutta, P. Chutia, J.D. Woollins and A.M.Z. Slawin, *Inorg. Chim. Acta*, 2006, **359**, 877]

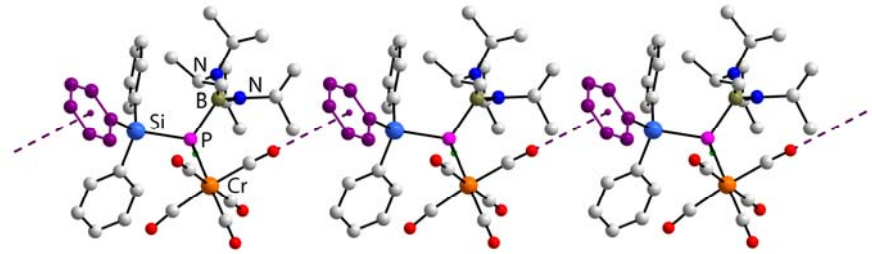


3.67 Å; 9.5°; 165.2°

CIWGUK10

Decacarbonyl-(μ_2-bis(N,N-diphenylphosphino)ethylamine-P,P')-triruthenium

[D.W. Engel, K.G. Moodley, L. Subramony and R.J. Haines, *J. Organomet. Chem*., 1988, **349**, 393]



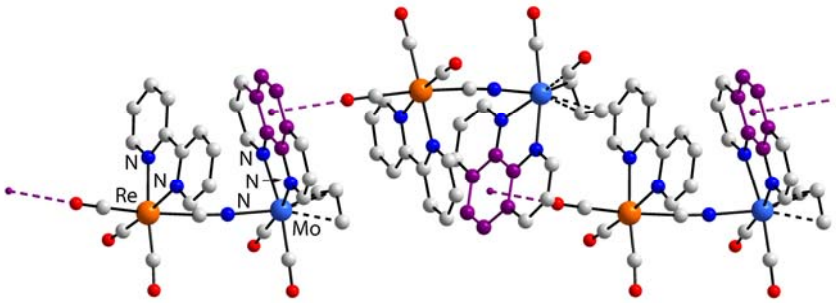
3.70 Å; 8.6°; 177.1°

WOFMEJ

((bis(Di-isopropylamino)boryl)(triphenylsilyl)phosphane)-pentacarbonylchromium

[T. Chen, J. Jackson, S.A. Jasper, E.N. Duesler, H. Noth and R.T. Paine, *J. Organomet. Chem*., 1999, **582**, 25]

MOTIF 6: Helical supramolecular chains sustained by a single M–carbonyl(lone pair)…π(aryl) interaction

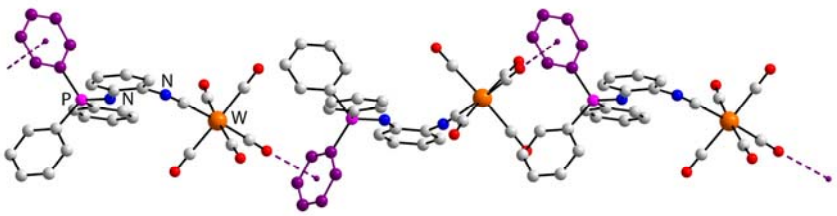


3.10 Å; 7.1°; 174.8°

MABQAI

(μ_2-Cyano)-(η^3-allyl)-(2,2'-bipyridyl)-pentacarbonyl-(1,10-phenanthroline)-molybdenum-rhenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate dichloromethane solvate

[J. Perez, E. Hevia, L. Riera, V. Riera, S.Garcia-Granda, E.Garcia-Rodriguez and D. Miguel, *Eur. J. Inorg. Chem*., 2003, 1113]

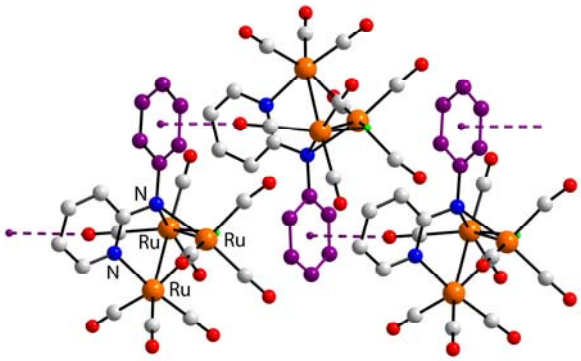


3.19 Å; 4.5°; 177.1°

XUZZOH

Pentacarbonyl-(2-(triphenylphosphinimino)phenyl isocyanide)-tungsten(0)

[F.E. Hahn, V. Langenhahn, N. Meier, T. Lugger and W.P. Fehlhammer, *Chem.-Eur. J.*, 2003, **9**, 704]

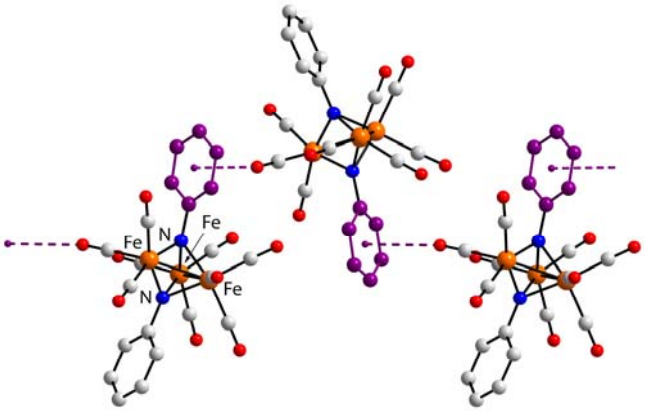


3.20 Å; 6.9°; 171.4°

JELYUU

1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2-(μ_2-hydrido)-(μ_3-phenyl(2'-pyridyl)amido-N,N,N')-tri-ruthenium

[P.L. Andreu, J.A. Cabeza, V. Riera, Y. Jeannin and D. Miguel, *J. Chem. Soc., Dalton Trans.* 1990, 2201]

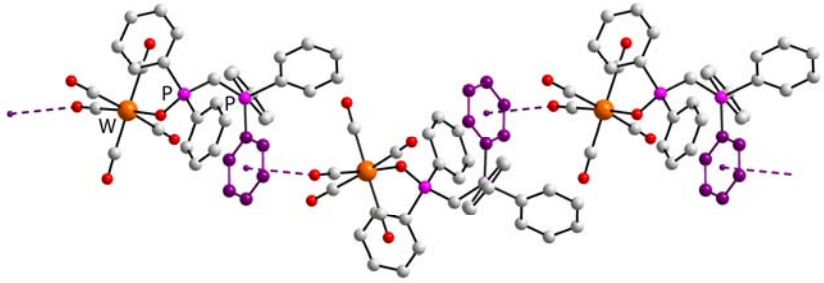


3.25 Å; 7.6°; 169.8°

COPHAQ

Nonacarbonyl-bis(μ_3-phenylimido)-tri-iron

[W. Clegg, G.M. Sheldrick, D. Stalke, S. Bhaduri and H.K. Khwaja, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1984, **40**, 2045]

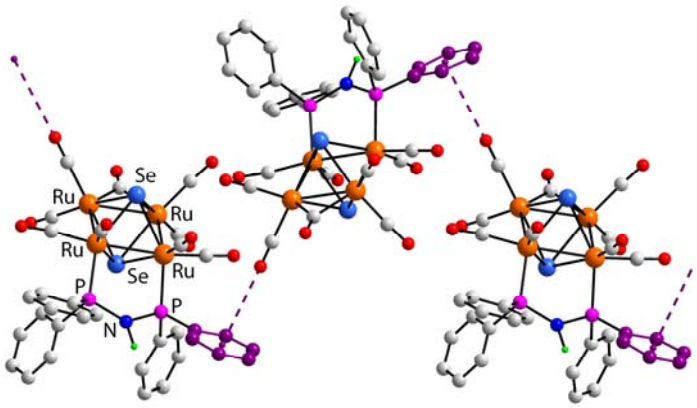


3.52 Å; 7.0°; 166.5°

PMYPCW

((Triphenylphosphinemethylide)diphenylphosphine oxide) pentacarbonyltungsten(0)

[S.Z. Goldberg and K.N. Raymond, *Inorg. Chem*., 1973, **12**, 2923]

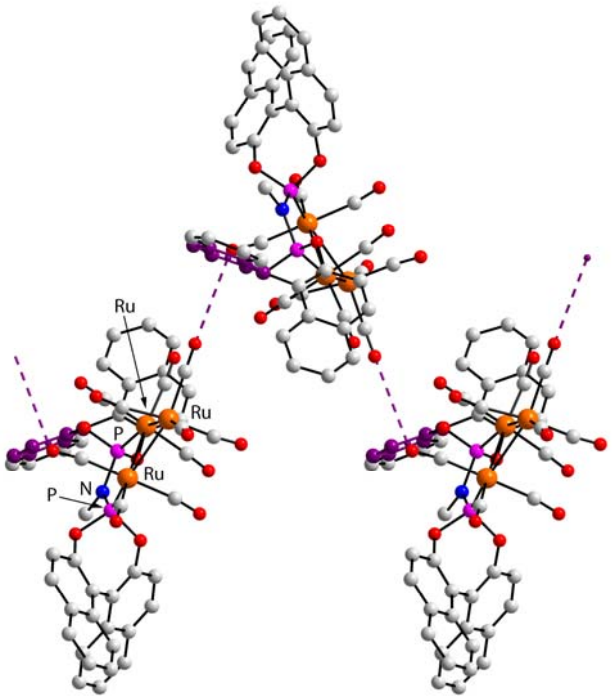


3.52 Å; 8.0°; 178.9°

NATFUJ

bis(μ_4-Selenido)-(μ_2-diphenyl(diphenylphosphinoimido)-phosphine)-(μ_2-carbonyl)-octacarbonyl-tetra-ruthenium hemihydrate

[A.M.Z. Slawin, M.B. Smith and J.D. Woollins, *J. Chem. Soc., Dalton Trans*., 1997, 1877]

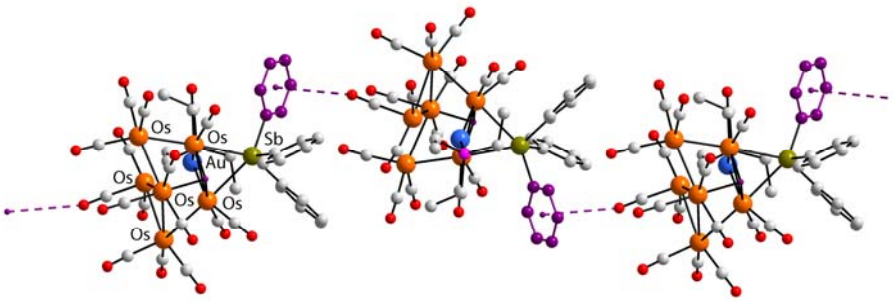


3.56 Å; 2.5°; 175.9°

NAFSOD

(S,S)-(μ_2-(N,N-bis(1,1'-binaphthylene-2,2'-dioxy)phosphino)methylamine)-decacarbonyl-tri-ruthenium

[T.S. Venkatakrishnan, M. Nethaji and S.S. Krishnamurthy, *Curr. Sci*., 2003, **85**, 969]



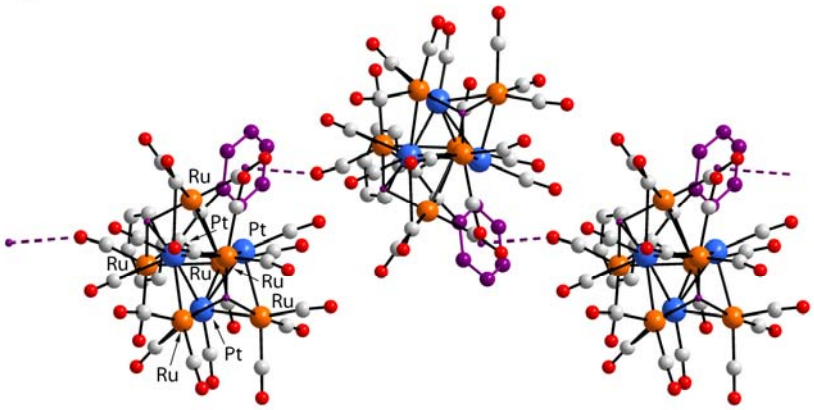
3.73 Å; 9.2°; 162.9°

IDEPOX

(μ_3-Hydrido)-hexadecacarbonyl-triethylphosphine-triphenyl-antimonygold-hexa-osmium

[P.G. Jones and P.R. Raithby, *Private Communication*, 2006]

MOTIF 7: Zig-zag supramolecular chains sustained by a single M–carbonyl(lone pair)…π(aryl) interaction

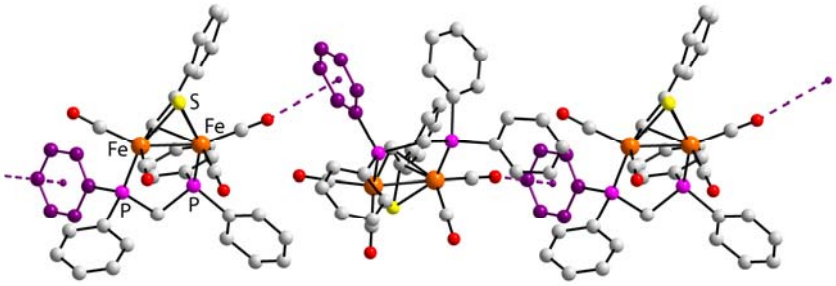


3.06 Å; 8.8°; 162.0°

JUTBIJ10

bis(μ_2-Hydrido)-(μ_3-η^2-diphenylethyne-1,1,2,2-diyl)-icosacarbonyl-triplatinum-hexa-ruthenium

[R.D. Adams, T.S. Barnard, Z. Li, W. Wu and J. Yamamoto, *Organometallics*, 1994,**13**, 2357]

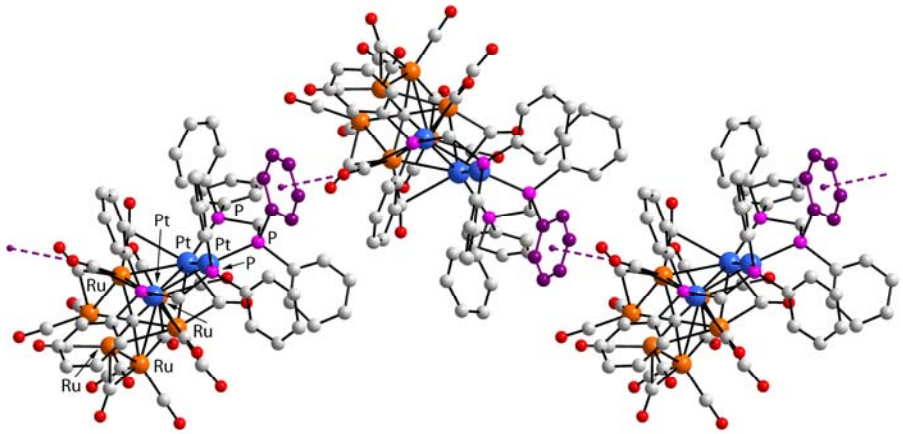


3.20 Å; 9.4°; 169.1°

IMOSIM

(μ_2-η^2-2-Mercapto-2-phenylethenyl-C,S,S)-(μ_2-bis(diphenylphosphino) methane-P,P')-tetracarbonyl-di-iron

[G. Hogarth, M.O' Brie and D.A. Tocher, *J. Organomet. Chem*., 2003, **672**, 22]

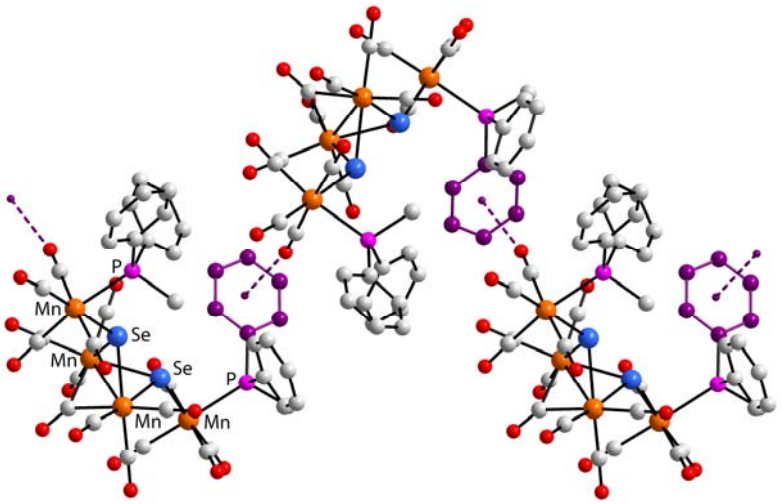


3.23 Å; 6.7°; 174.9°

QAHBEH

(μ_6-Carbido)-pentakis(μ_2-carbonyl)-bis(μ_2-bis(diphenylphosphino)methane)-undecacarbonyl-tri-platinum-hexa-ruthenium

[S. Hermans, T. Khimyak, N. Feeder, S.J. Teat and B.F.G. Johnson, *Dalton Trans*., 2003, 672]

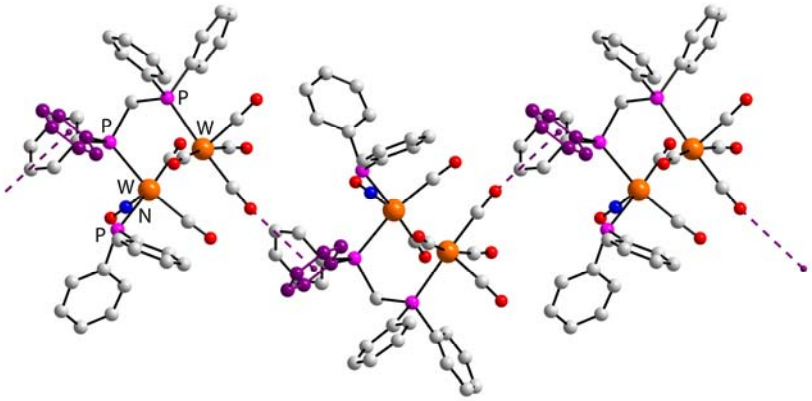


3.27 Å; 7.5°; 169.4°

EMUMOO

bis(μ_3-Selenido)-(μ_2-carbonyl)-tetradecacarbonyl-bis(diphenyl(methyl)phosphine)-tetra-manganese dichloromethane solvate

[D. Belletti, C. Graiff, C. Massera, R. Pattacini, G. Predieri and A. Tiripicchio, *Inorg. Chim. Acta*, 2003, **356**, 187]



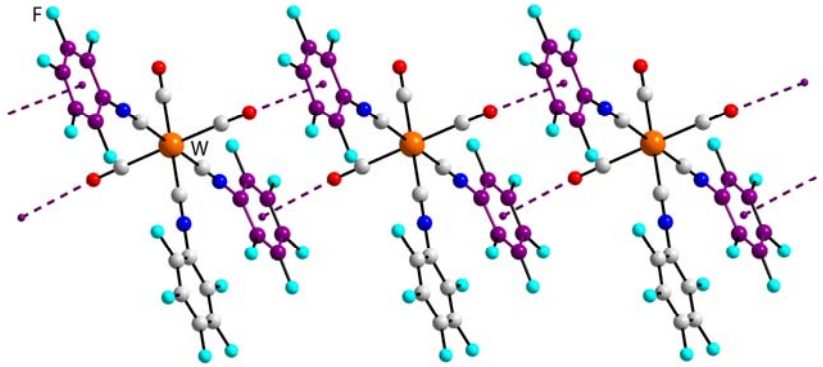
3.50 Å; 7.9°; 173.3°

JUCYOV

(μ_2-Hydrido)-(μ_2-bis(diphenylphosphino)methane)-hexacarbonylnitrosyl-(diphenylphosphino)-di-tungsten

[J. T.Lin, K.-Y. Chang, M. L.Gong, C.-C. Chang, H.-Mou Gau, L.-H. Tsen and Y. S. Wen, *J. Organomet. Chem*., 1992, **431**, 65]

MOTIF 8: Linear supramolecular chains sustained by a two M–carbonyl(lone pair)…π(aryl) interactions

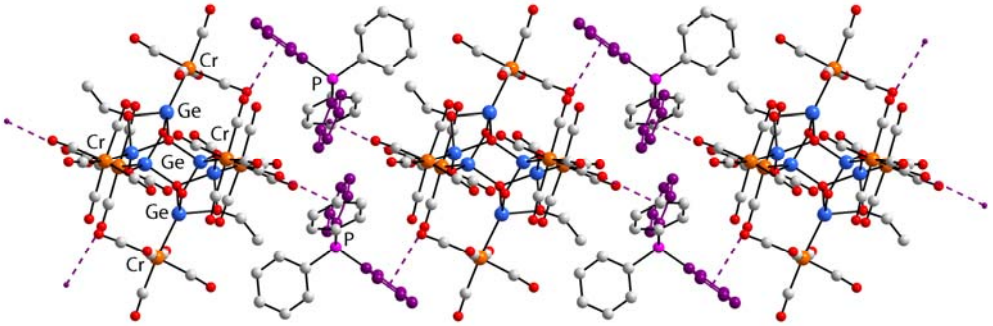


3.03 Å; 1.0°; 177.2°

BODNOX

mer-Tricarbonyl-tris(pentafluorophenyl isocyanide)tungsten

[D. Lentz, M. Anibarro, D. Preugschat and G. Bertrand, *J. Fluorine Chem*., 2004, **89**, 73]

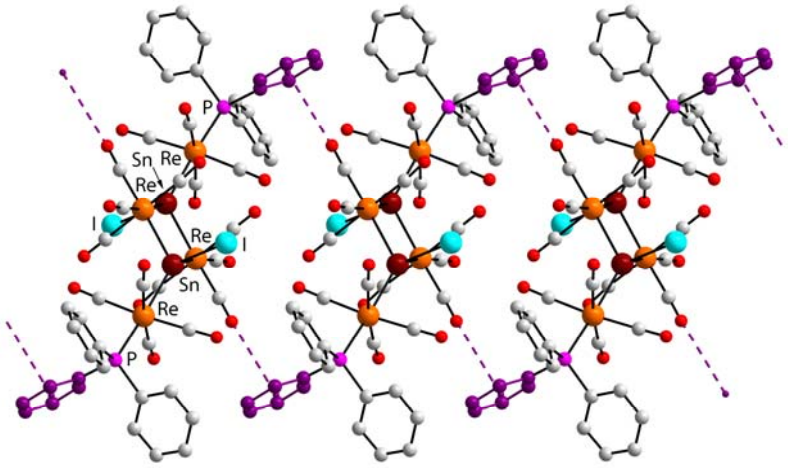


3.25 Å; 3.9°; 162.2° and 3.33 Å; 7.4°; 164.5°

ODEMUF

bis(Tetraphenylphosphonium) bis(μ_3-oxo)-bis(μ_2-ethoxo)-tetrakis(μ_2-oxo)-hexa-chromium-hexa-germanium

[G. Renner, G. Huttner and P. Rutsch, *Z. Naturforsch., B: Chem. Sci*., 2001, **56**, 1328]



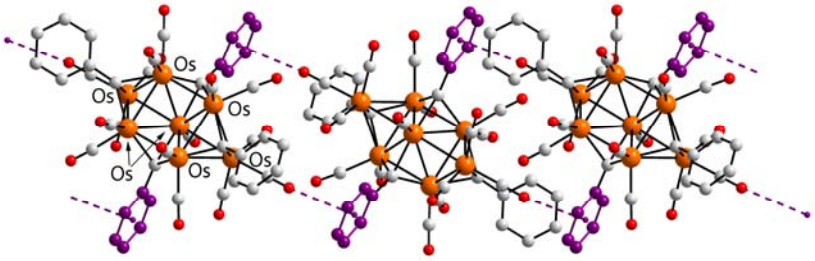
3.49 Å; 6.1°; 173.5°

CESRIB

Octacarbonyl-(μ$_2$-bis(iodo-(μ$_2$-tetracarbonyl-rhenium)-tin(iv)))- bis (triphenylphosphine-rhenium)

[H. Preut, H.-J. Haupt and U. Florke, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1984, **40**, 600]

MOTIF 9: Zig-zag supramolecular chains sustained by a two M–carbonyl(lone pair)…π(aryl) interactions



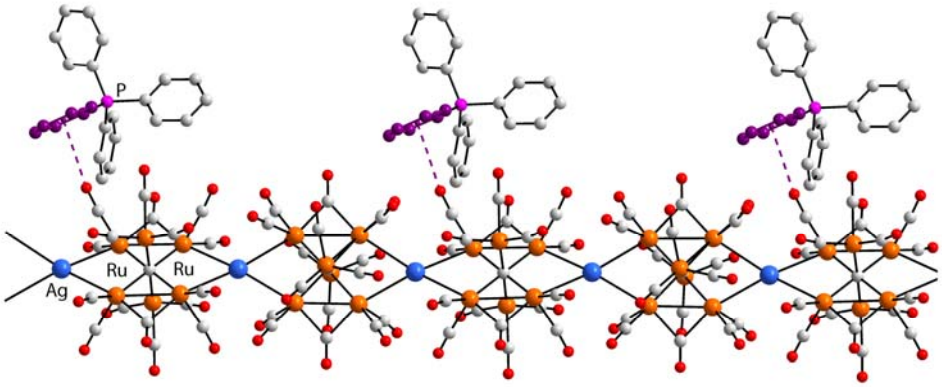
3.20 Å; 9.1°; 167.2°

GETMEX10

tetrakis(μ$_3$-Benzylidyne)-pentadecacarbonyl-hepta-osmium.

[D.Braga, F.Grepioni, B.F.G.Johnson, J.Lewis and J.Lunniss, *J. Chem. Soc., Dalton Trans,* 1991, 2223]

MOTIF 10: Linear polymer associated with counter cations via supramolecular M–carbonyl(lone pair)…π(aryl) interactions



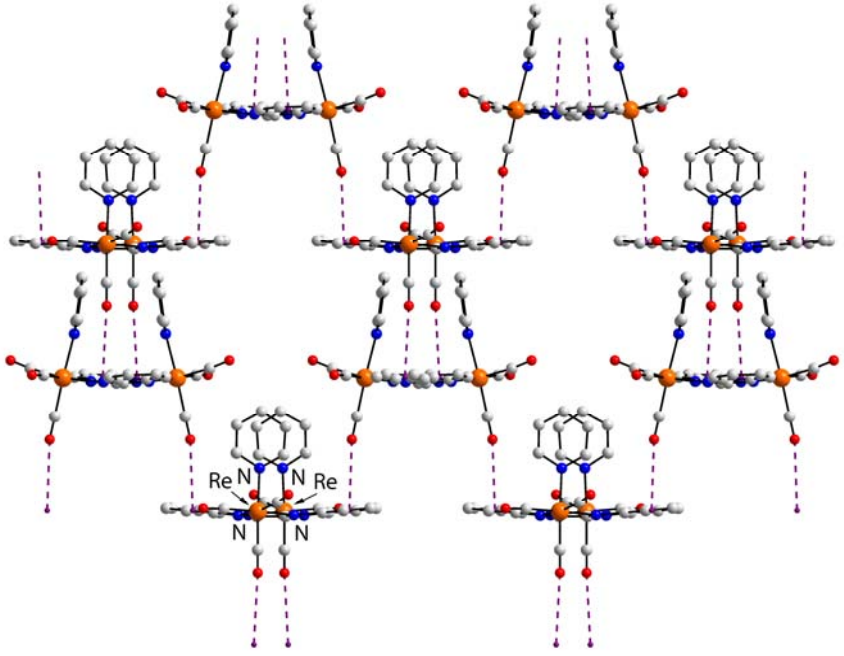
3.20 Å; 4.6°; 162.2°

QETZEU

catena-[bis(Triphenylphosphonium) bis(μ_6-carbido)-tetrakis(μ_2-carbonyl)-octacosacarbonyl-di-hexaruthenium-disilver]

[T. Nakajima, A. Ishiguro and Y. Wakatsuki, *Angew. Chem., Int. Ed*., 2001, **40**, 1066]

MOTIF 11: Three-dimensional architecture sustained by supramolecular M–carbonyl(lone pair)…π(aryl) interactions



3.49 Å; 7.3°; 169.2°

XAXTEW

trans-(μ_2-2,2'-Bisbenzimidazolyl)-hexacarbonyl-bis(pyridine)-di-rhenium(I)

[P.H. Dinolfo, K.D. Benkstein, C.L. Stern and J.T. Hupp, *Inorg. Chem*., 2005, **44**, 8707]

PART B: Plots of geometric parameters, α, β and *d*.

Figure S(1). Distribution of alpha (º) values.

Figure S(2). Distribution of beta (º) values.

Figure S(3). Distribution of d (Å) values.

Figure S(4). Plot of beta (º) versus alpha (º).

Figure S(5). Plot of alpha (º) versus d (Å).

Figure S(6). Plot of beta (º) versus d (Å).

Figure S(1). Distribution of alpha (º) values.

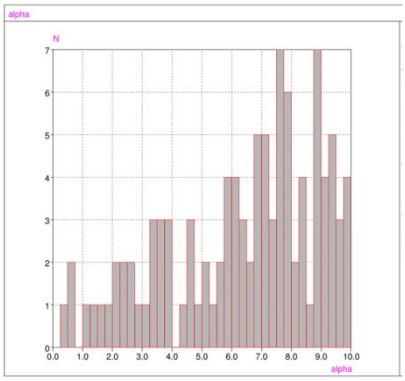


Figure S(2). Distribution of beta (º) values.

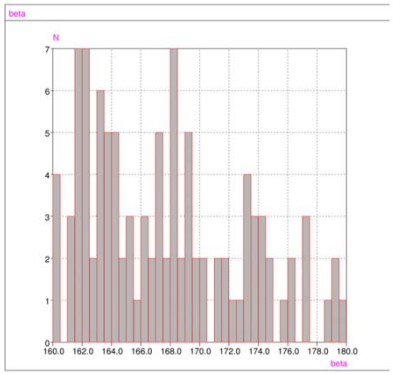


Figure S(3). Distribution of d (Å) values.

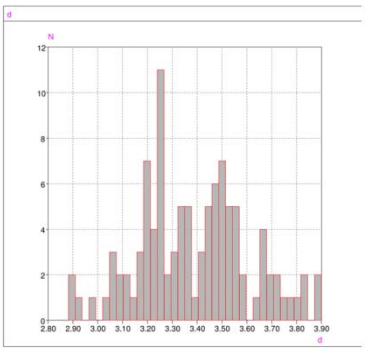


Figure S(4). Plot of beta (º) versus alpha (º).

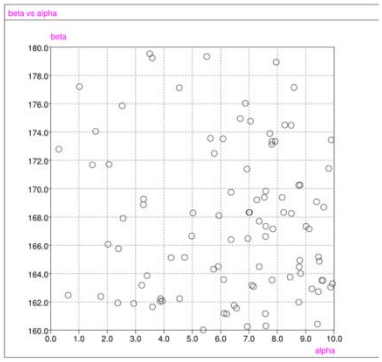


Figure S(5). Plot of alpha (º) versus d (Å).

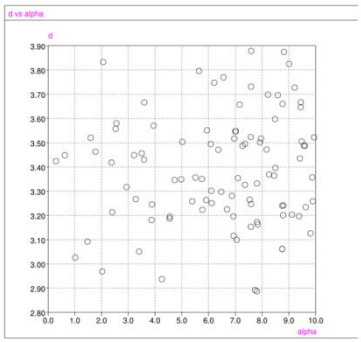


Figure S(6). Plot of beta (º) versus d (Å).