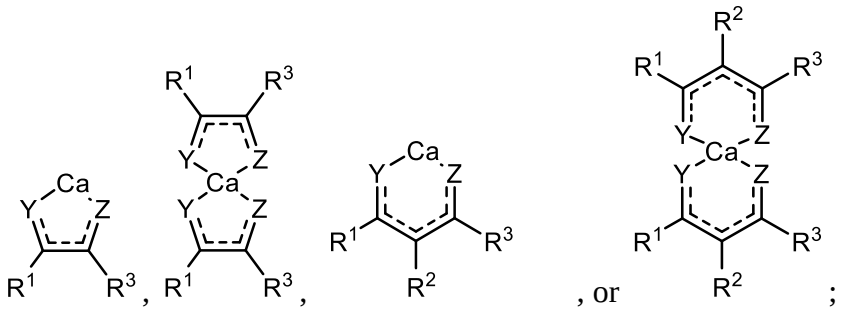
CLAIMS

What is claimed is:

1. A method of preventing or reducing low speed pre-ignition events in an internal combustion engine having a crankcase, comprising contacting the crankcase with a lubricating composition, comprising a base oil and at least one cyclic calcium chelate complex.

   wherein the calcium chelate complex comprises a complex having the formula:



   wherein:

   ⋮ independently represents a single or double bond, provided that valence is satisfied;

   Y is selected from O, S, or NR^{n1};

   Z is selected from O, S, or NR^{n2}; and

   R^1, R^2, R^3, R^{n1}, and R^{n2} are independently selected from R^a, OR^b, and $N(R^b)_2$;

   wherein R^a is in each case independently selected from hydrogen, C_{1-8} alkyl, C_{2-8} alkenyl, C_{2-8} alkynyl, aryl, C_{1-8} heteroaryl, C_{3-8} cycloalkyl, or C_{1-8} heterocyclyl; and

   R^b is in each case independently selected from C_{1-8} alkyl, C_{2-8} alkenyl, C_{2-8} alkynyl, aryl, C_{1-8} heteroaryl, C_{3-8} cycloalkyl, or C_{1-8} heterocyclyl

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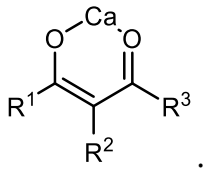
2. The method according to claim 1, wherein the calcium chelate complex has the formula:



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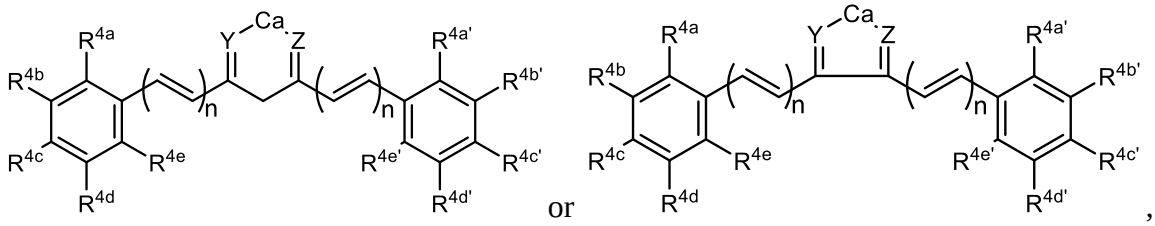
3. The method according to claim 1, wherein R^1 is selected from methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, tert-butoxy, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl.
4. The method according to claim 1, wherein R^3 is selected from methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, tert-butoxy, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl.
5. The method according to claim 1, wherein R^2 is selected from hydrogen, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, tert-butoxy, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl.
6. The method according to claim 1, wherein the calcium chelate complex has the formula:



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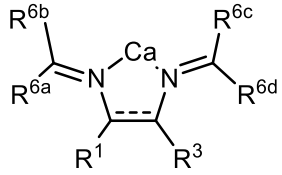
wherein n is 0, 1 or 2; and

R^{4a}, $R^{4a'}$, R^{4b}, $R^{4b'}$, R^{4c}, $R^{4c'}$, R^{4d}, $R^{4d'}$, R^{4e}, and $R^{4e'}$ are independently selected from hydrogen; hydroxy; $C_{1\text{-}22}$alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl; $C_{1\text{-}22}$O-alkyl, for instance methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, or tert-butoxy; wherein any two or more of R^{4a}, $R^{4a'}$, R^{4b}, $R^{4b'}$, R^{4c}, $R^{4c'}$, R^{4d}, $R^{4d'}$, R^{4e}, and $R^{4e'}$ can together form a ring, preferably R^{4c} and $R^{4c'}$ are either hydroxyl or amino, preferably R^{4b} and $R^{4b'}$ are each methoxy.

7. The method according to claim 1, wherein Y is NR^{n1}, and R^{n1} is $C_{1\text{-}8}$ alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl; $C_{1\text{-}8}$O-alkyl, for instance methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, or tert-butoxy.
8. The method according to claim 1, wherein Z is NR^{n2}, and R^{n2} is $C_{1\text{-}8}$ alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl; $C_{1\text{-}8}$O-

alkyl, for instance methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, or tert-butoxy.

9. The method according to claim 1, wherein Y is NR^{n1}, Z is NR^{n2}, and R^{n1} is C_{1-8} alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl, R^{n2} is C_{1-8}alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl, and R^2 is hydrogen or methyl.
10. The method according to claim 1, wherein the calcium complex has the formula:



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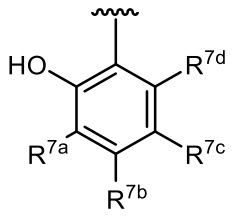
wherein R^{6a} and R^{6d} are independently selected from hydrogen or C_{1-8} alkyl, and R^{6b} and R^{6c} are each



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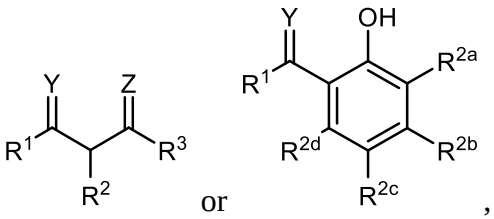
in which R^{7a}, R^{7b}, R^{7c}, and R^{7d} are independently selected from hydrogen, hydroxyl, C_{1-8} alkyl, and O-C_{1-8} alkyl; wherein any two or more of R^{7a}, R^{7b}, R^{7c}, and R^{7d} can together form a ring.

11. A method of preventing or reducing low speed pre-ignition events in an internal combustion engine having a crankcase, comprising contacting the crankcase with a lubricating composition, comprising a base oil and at least one cyclic chelate complex, wherein the cyclic calcium chelate complex is the reaction product a calcium compound and a ligand having the formula:



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wherein

Y is selected from O, S, NR^{n1};

Z is selected from O, S, NR^{n2};

R^1, R^2, R^3, R^{n1}, and R^{n2} are independently selected from R^a, OR^b, and $N(R^b)_2$;

wherein R^a is in each case independently selected from hydrogen, C_{1-8} alkyl, C_{2-8} alkenyl, C_{2-8} alkynyl, aryl, C_{1-8} heteroaryl, C_{3-8} cycloalkyl, or C_{1-8} heterocyclyl;

R^b is in each case independently selected from C_{1-8}alkyl, C_{2-8}alkenyl, C_{2-8}alkynyl, aryl, C_{1-8}heteroaryl, C_{3-8}cycloalkyl, or C_{1-8}heterocyclyl; and

wherein R^{2a}, R^{2b}, R^{2c}, and R^{2d} are independently selected from hydrogen; hydroxy; C_{1-22}alkyl; and O-C_{1-22}alkyl

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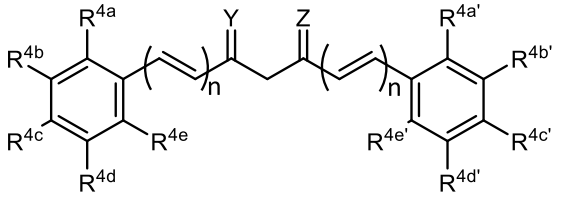
12. A method of preventing or reducing low speed pre-ignition events in an internal combustion engine having a crankcase, comprising contacting the crankcase with a lubricating composition, comprising a base oil and at least one cyclic chelate complex, wherein the calcium chelate complex is the reaction product of a calcium compound and a ligand compound having the formula:



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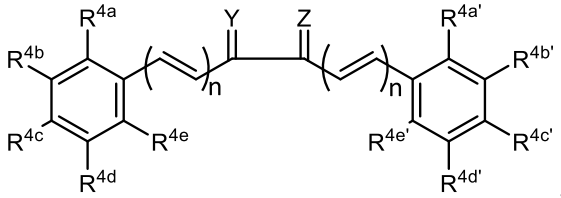

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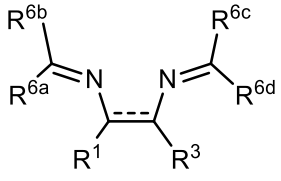
wherein n is 0, 1 or 2; and R^{4a}, $R^{4a'}$, R^{4b}, $R^{4b'}$, R^{4c}, $R^{4c'}$, R^{4d}, $R^{4d'}$, R^{4e}, and $R^{4e'}$ are independently selected from hydrogen; hydroxy; C_{1-22}alkyl, for instance, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, and tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl; C_{1-22}O-alkyl, for instance methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, or tert-butoxy; and preferably R^{4c} and $R^{4c'}$ are either hydroxyl or amino, preferably R^{4b} and $R^{4b'}$ are each methoxy.

13. The method according to claim 1, wherein the calcium chelate complex is the reaction product of a calcium compound and a ligand compound having the formula:



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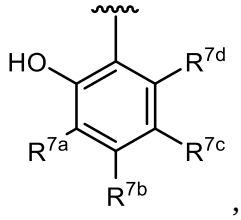
wherein R^{6a} and R^{6d} are independently selected from hydrogen or $C_{1\text{-}8}$alkyl, and R^{6b} and R^{6c} are each



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in which R^{7a}, R^{7b}, R^{7c}, and R^{7d} are independently selected from hydrogen, hydroxyl, $C_{1\text{-}8}$alkyl, and O-$C_{1\text{-}8}$alkyl; wherein any two or more of R^{7a}, R^{7b}, R^{7c}, and R^{7d} can together form a ring.

14. The method according to claim 11, wherein the molar ratio of calcium compound to ligand compound is about 1:1, 1:2, or 1:3.
15. The method according to claim 11, wherein the calcium compound comprises a calcium base.
16. The method according to claim 11, wherein the calcium compound comprises a calcium salt.
17. The method according to claim 1, wherein the calcium chelate compound is present in about an amount from 100 – 3,000 ppm, from 200 to 3,000 ppm, or from 250 to 2,500 ppm, from 300 to 2,500 ppm, from 350 to 2,500 ppm, from 400 to 2,500 ppm, from 500 to 2,500 ppm, from 600 to 2,500 ppm, from 700 to 2,500 ppm, from 700 to 2,000 ppm, or from 700 to 1,500 ppm.
18. The method of any one of claims 1-17, wherein the internal combustion engine is a spark-ignited internal combustion engine.
19. The method of claim 18, wherein the internal combustion engine experiences no more than 90%, no more than 80%, no more than 70%, no more than 60%, no more than 50%, no more than 40%, no more than 30%, no more than 20%, no more than 10%, or no more than 5% of the low speed pre-ignition events experienced by an internal combustion engine lubricated with an otherwise same lubricating composition that does not include the calcium cyclic chelate complex.
20. The method of claim 18, wherein the internal combustion engine experiences no more than 10 LSPI events over at least 100,000 combustion cycles, no more than 8 LSPI events over at least 100,000 combustion cycles, no more than 6 LSPI events over at least 100,000 combustion cycles, no more than 4 LSPI events over at least 100,000

combustion cycles, no more than 2 LSPI events over at least 100,000 combustion cycles, or no more than 1 LSPI event over at least 100,000 combustion cycles.